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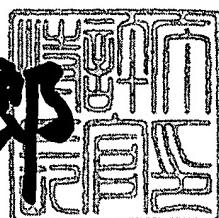
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2003年 6月30日

特許庁長官  
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Japan Patent Office

太田 信一郎



出証番号 出証特2003-3051674

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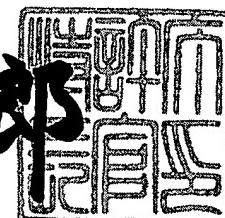
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出証番号 出証特2003-3051672

DECLARATION

I, Chieko Kosuge, a staff member of TAIYO, NAKAJIMA & KATO, 3-17, Shinjuku 4-chome, Shinjuku-ku, Tokyo 160-0022, Japan, do hereby declare that I am well acquainted with the English and Japanese languages and I hereby certify that, to the best of my knowledge and belief, the following is a true and correct translation made by me into the English language of the documents in respect of Japanese Patent Application No. 2002-287818, that was filed on 30th September 2002 in the name of FUJI PHOTO FILM CO., LTD.

Dated this 5th day of July, 2005



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Chieko Kosuge

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[CONSIGNEE] The Director General of the Patent Office  
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[LIST OF FILED DOCUMENT]

[DOCUMENT]	Specification	1
[DOCUMENT]	Abstract of the Disclosure	1
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[DOCUMENT NAME] SPECIFICATION

[TITLE OF THE INVENTION]

IMAGE FORMING MATERIAL

[CLAIMS]

[Claim 1] An image forming material comprising a support and an image forming layer which is laminated on the support and contains at least (A) a water-insoluble and alkali-soluble high-molecular compound and (B) a compound having a structure represented by the following general formula (1) and having an absorption maximum at a wavelength in a range of 760 nm to 1,200 nm:

General formula (1):  $X^-M^+$

wherein in the general formula (1),  $X^-$  represents an anion containing at least one substituent having an alkali-dissociating proton; and  $M^+$  represents a counter cation which is an atomic group having an absorption maximum at a wavelength in a range of 760 nm to 1,200 nm.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Industrial Field of the Invention]

The present invention relates to an image forming material that can be used as an offset printing master, and particularly to a positive image forming material useful as a positive planographic printing plate precursor for an infrared laser for so-called direct plate making in which plate making can be

performed directly from digital signals from computers, and the like.

[0002]

[Prior Art]

In recent years, development of lasers has been remarkable. In particular, with respect to solid lasers or semiconductor lasers having an emitting region in the near infrared to infrared wavelength region, high-output and small-sized products have become easily available. In a field of planographic printing plates, these lasers are very useful as exposure light sources during direct plate making from digital data form computers, and the like.

[0003]

As a positive photosensitive image forming materials for an infrared laser for direct plate making, which have hitherto been known, a positive photosensitive image forming material in which a light-heat converting substance that absorbs light to generate heat and a positive photosensitive compound, such as various onium salts or quinonediazide compounds, are added to a water-insoluble and alkali-soluble high-molecular compound (hereinafter properly referred to as "alkali-soluble resin") (see patent document 1 below). These positive photosensitive compounds work as a dissolution inhibitor that substantially lowers solubility of an image forming layer due to an interaction with the alkali-soluble resin in image areas (unexposed areas). In

non-image areas (exposed areas), the above-described positive photosensitive compounds are decomposed by heat and do not exhibit a dissolution inhibiting ability, and the non-image areas can be removed by development to form an image.

[0004]

As alkali-soluble resins to be used in such positive image forming materials, phenolic hydroxyl group-containing novolac resins are suitably used. The novolac resins are especially preferably used for the reasons that they strongly mutually act with the above-described dissolution inhibitor so that a difference between solubilities in developing solutions at exposed areas and unexposed areas is large and that they are excellent in ink receptivity.

[0005]

Further, positive photosensitive image forming materials are disclosed which each comprise a substance that absorbs light to generate heat and a resin whose solubility in alkaline aqueous solutions is changed by heat. Such image forming materials are low in solubility in alkaline aqueous solutions at image areas and high in solubility in alkaline aqueous solutions at non-image areas, and the non-image areas can be removed by development to form an image.

[0006]

As the dissolution inhibitor, a wide variety of compounds have been investigated. Among infrared (IR) absorbing materials

that play an important role by exhibiting a light-heat converting ability in infrared-sensitive image forming materials, ones having a strong dissolution inhibiting ability are known, and such compounds receive attention because they have dual functions together. In particular, IR coloring materials having a cation site in the molecule thereof have a strong mutual action with novolac resins, etc. and exhibit a high dissolution inhibiting ability. However, these coloring materials have a problem such that, although they exhibit an enhancing effect of dissolution inhibiting ability in image areas (unexposed areas), when an addition amount thereof increases, solubility in alkalis in non-image areas (exposed areas) lowers so as to increase an amount of energy necessary for removing the non-image areas, leading to a reduction in sensitivity. On the other hand, IR coloring materials are an essential material for thermal image formation, and when an addition amount thereof is too small, light-heat converting ability is reduced, and therefore, there are limits to the degree to which the addition amount can be controlled to adjust image forming property, which presents an obstacles to enhancement of sensitivity.

[0007]

[Patent document 1]

Japanese Patent Application Laid-open (JP-A) No. 7-285275

[Patent document 2]

International Publication WO 97/39894

[Patent document 3]

EP Patent Application Publication (EP-A) No. 0823327A2

[0008]

[Problems to be solved by the Invention]

Accordingly, an object of the present invention is to provide an image forming material having a large difference between solubilities in developing solutions at exposed areas and unexposed areas and being useful as a high-sensitivity heat mode type positive planographic printing plate precursor. The difference in solubility in developing solutions between exposed areas and unexposed areas will be hereinafter properly referred to as "solubility discrimination".

[0009]

[Means for solving the Problems]

Under such circumstances, the present inventors made extensive and intensive investigations. As a result, it has been found that by including a specific IR coloring material in an image forming layer, it is possible to achieve excellent solubility discrimination together with high sensitivity, which led to accomplishment of the present invention.

[0010]

Specifically, the image forming material of the present invention is concerned with an image forming material comprising a support and an image forming layer which is laminated on the support and contains at least (A) a water-insoluble and

alkali-soluble high-molecular compound and (B) a compound having a structure represented by the following general formula (1) and having an absorption maximum at a wavelength in a range of 760 nm to 1,200 nm:

General formula (1):  $X^-M^+$

wherein in the general formula (1),  $X^-$  represents an anion containing at least one substituent having an alkali-dissociating proton; and  $M^+$  represents a counter cation which is an atomic group having an absorption maximum at a wavelength in a range of 760 nm to 1,200 nm.

[0011]

The exact mechanism resulting in the effects of the present invention is not completely clear but is presumed to be as follows.

That is, in general, when a compound containing an alkali-dissociating substituent, such as a phenolic hydroxyl group, a carboxyl group, or a mercapto group, is added to an image forming layer, the compound functions as a dissolution accelerator, whereby its dissolution inhibiting ability in unexposed areas is lowered. However, in the compound having a structure represented by the above-described general formula (1) and having an absorption maximum at a wavelength ranging from 760 nm to 1,200 nm (this compound being hereinafter properly referred to as a "specific IR coloring material"), such an alkali-dissociating substituent is present on a counter anion, and the compound has an infrared absorbing ability, and a cation

matrix having a structure as a dissolution inhibitor does not have a structure that lowers such a dissolution inhibiting ability. Accordingly, in image areas (unexposed areas), it is possible to keep high resistance to alkaline dissolution without substantially deteriorating the dissolution inhibiting ability derived from the structure of the IR pigment. This is because in the unexposed areas, the water-insoluble and alkali-soluble high-molecular compound (alkali-soluble resin) (A) forms a strong mutual action with the cation segment of the specific IR coloring material and surrounds the whole of the molecule of the specific IR coloring material so as to cover it.

[0012]

On the other hand, in the exposed areas, it is thought that flexibility of the matrix increases due to strong heat generation, and at this moment, a degree of freedom of movement in a film enhances. In this specific IR coloring material, since the counter anion is not covalently fixed but only ionically bonded to the cation matrix, the degree of freedom of movement is high so that a large change of alignment is likely caused. For this reason, the alkali-dissociating substituent present in the counter anion functions effectively, whereby release of the alkali dissolution inhibiting ability is rapidly carried out. Moreover, in the specific IR coloring material according to the invention, the cation matrix site itself has a photothermal converting ability, and it is estimated that this change takes place in the surroundings of the

molecule with extremely good efficiency. It is thought that high sensitivity and high discrimination are realized as a result thereof.

[0013]

Incidentally, the term "heat mode type" as referred to in the invention means that recording by heat mode exposure can be carried out.

The definition of the heat mode exposure in the invention, will be described in detail. As described on page 209 of *Hans-Joachim Timpe, IS&Ts NIP 15:1999, International Conference on Digital Printing Technologies*, it is known that in photosensitive materials, when a light-absorbing substance (for example, a dye) is photo-excited to form an image via a chemical or physical change, there are roughly two modes in the process from photo-excitation of the light-absorbing substance to the chemical or physical change. One mode is a so-called photon mode in which the photo-excited light-absorbing substance is deactivated by some photochemical mutual action (for example, energy transfer or electron transfer) with other reactive substances in the photosensitive material, and as a result, the activated reactive substance causes a chemical or physical change necessary for the above-described image formation. The other mode is a so-called heat mode in which the photo-excited light-absorbing substance is deactivated by the generation of a heat, and the reactive substance causes a chemical or physical change necessary for the above-described image formation while utilizing the generated

heat. In addition, there are also special modes such as ablation in which the substance explosively flies about due to locally concentrated light energy and multimolecular absorption in which one molecule absorbs a number of photons all at once, but such special modes are omitted herein.

[0014]

The exposure processes utilizing each of the above-described modes are referred to as "photon mode exposure" and "heat mode exposure", respectively. A technical difference between the photon mode exposure and the heat mode exposure resides in whether an energy amount of several photons to be exposed can be added to an energy amount of the desired reaction and used. For example, causing a certain reaction using  $n$  photons will be considered. In the photon mode exposure, since a photochemical mutual action is utilized, it is impossible, according to the demands of the laws of conservation of quantum energy and momentum, to add the energy of one photon and use it. Namely, in order to cause some reaction, a relation of "(energy amount of one photon)  $\geq$  (energy amount of reaction)" is necessary. On the other hand, in the heat mode exposure, since heat is generated after photo-excitation, and light energy is converted to heat and utilized, it is possible to add an energy amount. For this reason, it is sufficient if a relation of "(energy amount of  $n$  photons)  $\geq$  (energy amount of reaction)" is present. However, the addition of this energy amount is restricted by thermal diffusion. That is, if a

next photo-excitation-to-deactivation step takes place to generate a heat by the time until heat escapes from an exposed portion (reaction point), which is the present point of concern, due to thermal diffusion, the heat is surely accumulated and added, leading to a temperature elevation in that portion. However, in the case where next heat generation is slow, the heat escapes and is not accumulated. Namely, in the heat mode exposure, even if the entire exposure energy amount is identical, the result is different between the case where light having a high energy amount is irradiated for a short period of time and the case where light having a low energy amount is irradiated for a long period of time, and the short-period irradiation is advantageous for heat accumulation.

[0015]

As a matter of course, in the photon mode exposure, a similar phenomenon may occurs due to influences of diffusion of subsequent reaction seeds, but basically the above-described phenomenon does not take place.

Namely, when characteristics of photosensitive material are concerned, according to the photon mode, an inherent sensitivity (energy amount for reaction necessary for image formation) of the photosensitive material against an exposure power density ( $\text{W/cm}^2$ ) (= energy density per unit time) is constant, whereas according to the heat mode, the inherent sensitivity of the photosensitive material relative to the exposure

power density increases. Accordingly, when the respective modes are compared while fixing an exposure time to an extent such that productivity necessary for actual image forming materials can be maintained from the standpoint of practical use, according to the photon mode exposure, a high sensitivity of about  $0.1 \text{ mJ/cm}^2$  can be usually achieved, but since the reaction occurs even at a low exposure amount, a problem of low-exposure fogging in unexposed areas is liable to occur. On the other hand, according to the heat mode exposure, the reaction does not take place unless the exposure amount exceeds a certain amount. Further, an exposure amount of about  $50 \text{ mJ/cm}^2$  is usually required due to the relationship with thermal stability of the photosensitive material, but the problem of low-exposure fogging is avoided.

Further, according to the heat mode exposure, an exposure power density of  $5,000 \text{ W/cm}^2$  or more, and preferably  $10,000 \text{ W/cm}^2$  or more is actually required on a printing plate surface of the photosensitive material. However, although the details have not been described herein, when a high-power density laser of  $5.0 \times 10^5 \text{ W/cm}^2$  or more is utilized, ablation takes place to bring about problems such as staining of light sources, and hence, such is not preferred.

[0016]

[Embodiments]

The present invention will be described in detail below.

The image forming material of the invention is necessary to

contain as components of an image forming layer (A) a water-insoluble and alkali-soluble high-molecular compound and (B) a compound having a structure represented by the following general formula (1) and having an absorption maximum at a wavelength in a range of 760 nm to 1,200 nm. Each of the components constituting the image forming layer in the image forming material of the invention will be hereunder described one by one.

[0017]

[(B) Compound having a structure represented by the general formula (1) and having an absorption maximum at a wavelength in a range of 760 nm to 1,200 nm]

The image forming layer according to the present invention contains a compound (specific IR absorbing material) having a structure represented by the following general formula (1) and having an absorption maximum at a wavelength in a range of 760 nm to 1,200 nm.

General formula (1):  $X^-M^+$

[0018]

In the general formula (1),  $X^-$  represents an anion containing at least one substituent having an alkali-dissociating proton. Suitable examples of such substituents having an alkali-dissociating proton that can be used include a phenolic hydroxyl group ( $Ar-OH$ ), a carboxyl group ( $-COOH$ ), a mercapto group ( $-SH$ ), a phosphonic acid group ( $-PO_3H_2$ ), a phosphoric acid

group (-OPO<sub>3</sub>H<sub>2</sub>), a sulfonamide group (-SO<sub>2</sub>NH<sub>2</sub> and -SO<sub>2</sub>NHR), a substituted sulfonamide based group (hereinafter referred to as "active imide group"; -SO<sub>2</sub>NHCOR, -SO<sub>2</sub>NHSO<sub>2</sub>R, and -CONHSO<sub>2</sub>R), a sulfonic acid group (-SO<sub>3</sub>H), a sulfinic acid group (-SO<sub>2</sub>H), -C(CF<sub>3</sub>)<sub>2</sub>OH, and -COCH<sub>2</sub>COCF<sub>3</sub>. Here, Ar represents an optionally substituted aryl group, and R represents an optionally substituted hydrocarbon group. As systems having a good balance between the dissolution inhibiting ability and the sensitivity, can be enumerated a phenolic hydroxyl group, a carboxyl group, a mercapto group, a sulfonamide group, an active imide group, -C(CF<sub>3</sub>)<sub>2</sub>OH, and -COCH<sub>2</sub>COCF<sub>3</sub>, with a phenolic hydroxyl group and a carboxyl group being the most preferred.

[0019]

X<sup>-</sup> is preferably an anion corresponding to a conjugated base of a Bronsted acid, and more preferably an anion corresponding to a conjugated base of an organic acid. Though the organic acid can be selected from sulfonic acid, carboxylic acids, phosphonic acid, phenols, active imides, and sulfinic acid, acids of pKa < 3 are preferable, acids of pKa < 1 are more preferable, and sulfonic acid is particularly preferable.

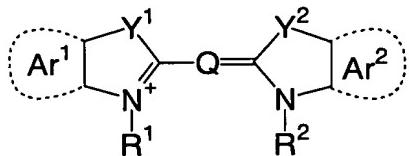
[0020]

In the general formula (1), M<sup>+</sup> represents a counter cation which is an atomic group having an absorption maximum at a wavelength in a range of 760 nm to 1,200 nm. As the structure of M<sup>+</sup>, structures represented by the following general formulae (a<sup>+</sup>),

(c<sup>+</sup>), (d<sup>+</sup>), (f<sup>+</sup>-1) and (f<sup>+</sup>-2) are preferable because they are excellent in light-heat conversion efficiency. Especially, cyanine dyes represented by the general formula (a<sup>+</sup>) are the most preferable because they give a high mutual action with the alkali-soluble resin (A) described later and are excellent in stability and economy.

[0021]

General formula (a<sup>+</sup>)



[0022]

In the general formula (a<sup>+</sup>), R<sup>1</sup> and R<sup>2</sup> each independently represents an alkyl group having from 1 to 12 carbon atoms, which may have a substituent selected from an alkoxy group, an aryl group, an amide group, an alkoxy carbonyl group, a hydroxyl group, a sulfo group, and a carboxyl group. Y<sup>1</sup> and Y<sup>2</sup> each independently represents an oxygen atom, a sulfur atom, a selenium atom, a dialkylmethylene group, or -CH=CH-. Ar<sup>1</sup> and Ar<sup>2</sup> each independently represents an aromatic hydrocarbon group, which may have a substituent selected from an alkyl group, an alkoxy group, a halogen atom, and an alkoxy carbonyl group, and may fuse the aromatic ring together with Y<sup>1</sup> or Y<sup>2</sup> and two carbon atoms adjacent thereto.

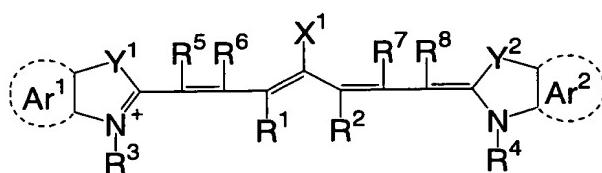
[0023]

In the general formula (a<sup>+</sup>), Q represents an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, a dialkylamino group, a diarylamino group, a halogen atom, an alkyl group, an aralkyl group, a cycloalkyl group, an aryl group, an oxy group, or an iminium salt group. Suitable examples of substituents as Q include halogen atoms such as a chlorine atom, diarylamino groups such as a diphenylamino group, and arylthio groups such as a phenylthio group.

[0024]

Among the cyanine dyes represented by the general formula (a<sup>+</sup>), in the case of exposure with an infrared ray having a wavelength from 800 to 840 nm, heptamethinecyanine dyes represented by the following general formulae (a<sup>+-1</sup>) to (a<sup>+-3</sup>) can be preferably enumerated.

[0025]



General formula (a<sup>+-1</sup>)

[0026]

In the general formula (a<sup>+-1</sup>), X<sup>1</sup> represents a hydrogen atom or a halogen atom. R<sup>1</sup> and R<sup>2</sup> each independently represents

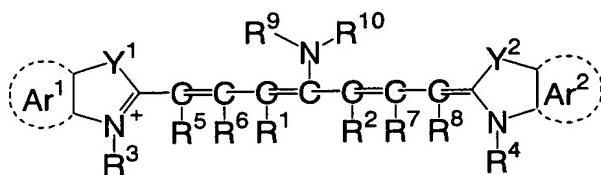
a hydrocarbon group having from 1 to 12 carbon atoms. R<sup>1</sup> and R<sup>2</sup> are preferably a hydrocarbon group having two or more carbon atoms from the standpoint of storage stability of coating solutions for image forming layer. Further, it is particularly preferred that R<sup>1</sup> and R<sup>2</sup> are taken together to form a 5-membered or 6-membered ring.

[0027]

In the general formula (a<sup>+-1</sup>), Ar<sup>1</sup> and Ar<sup>2</sup> may be the same or different and each represents an optionally substituted aromatic hydrocarbon group. Preferred examples of aromatic hydrocarbon groups include a benzene ring and a naphthalene ring. Preferred examples of substituents include hydrocarbon groups having not more than 12 carbon atoms, halogen atoms, and alkoxy groups having not more than 12 carbon atoms. Y<sup>1</sup> and Y<sup>2</sup> may be the same or different and each represent a sulfur atom or a dialkylmethylene group having not more than 12 carbon atoms. R<sup>3</sup> and R<sup>4</sup> may be the same or different and each represent an optionally substituted hydrocarbon group having not more than 20 carbon atoms. Preferred examples of substituents include alkoxy groups having not more than 12 carbon atoms, a carboxyl group, and a sulfo group. R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> may be the same or different and each represent a hydrogen atom or a hydrocarbon group having not more than 12 carbon atoms, with a hydrogen atom being preferred from the standpoint of easiness of availability of raw materials.

[0028]

General formula (a<sup>+-2</sup>)

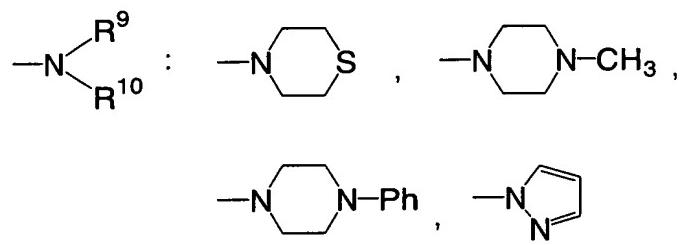


[0029]

In the general formula (a<sup>+-2</sup>), R<sup>1</sup> and R<sup>2</sup> each independently represents a hydrogen atom or a hydrocarbon group having from 1 to 12 carbon atoms, and R<sup>1</sup> and R<sup>2</sup> may bond with each other to form a ring structure. As the ring formed by R<sup>1</sup> and R<sup>2</sup>, 5-membered or 6-membered rings are preferable, and 5-membered rings are particularly preferable. Ar<sup>1</sup> and Ar<sup>2</sup> may be the same or different and each represent an optionally substituted aromatic hydrocarbon group. Preferred examples of aromatic hydrocarbon groups include a benzene ring and a naphthalene ring. Preferred examples of substituents on the aromatic hydrocarbon group include hydrocarbon groups having not more than 12 carbon atoms, halogen atoms, and alkoxy groups, alkoxy carbonyl groups, alkylsulfonyl group and halogenated alkyl groups each having not more than 12 carbon atoms, with electron-withdrawing substituents being particularly preferred. Y<sup>1</sup> and Y<sup>2</sup> may be the same or different and each represent a sulfur atom or a dialkylmethylene group having not more than 12 carbon

atoms. R<sup>3</sup> and R<sup>4</sup> may be the same or different and each represent an optionally substituted hydrocarbon group having not more than 20 carbon atoms. Preferred examples of substituents include alkoxy groups having not more than 12 carbon atoms, a carboxyl group, and a sulfo group. R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> may be the same or different and each represent a hydrogen atom or a hydrocarbon group having not more than 12 carbon atoms, with a hydrogen atom being preferred from the standpoint of easiness of availability of raw materials. R<sup>9</sup> and R<sup>10</sup> may be the same or different and each represent an optionally substituted aromatic hydrocarbon group having from 6 to 10 carbon atoms, an alkyl group having from 1 to 8 carbon atoms, or a hydrogen atom, or R<sup>9</sup> and R<sup>10</sup> may bond with each other to form a ring having any one of the following structures.

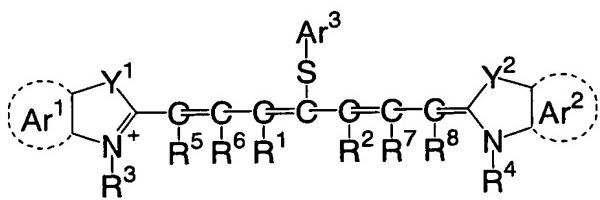
[0030]



[0031]

In the general formula  $(a^+ - 2)$ ,  $R^9$  and  $R^{10}$  are most preferably an aromatic hydrocarbon group such as a phenyl group.

[0032]

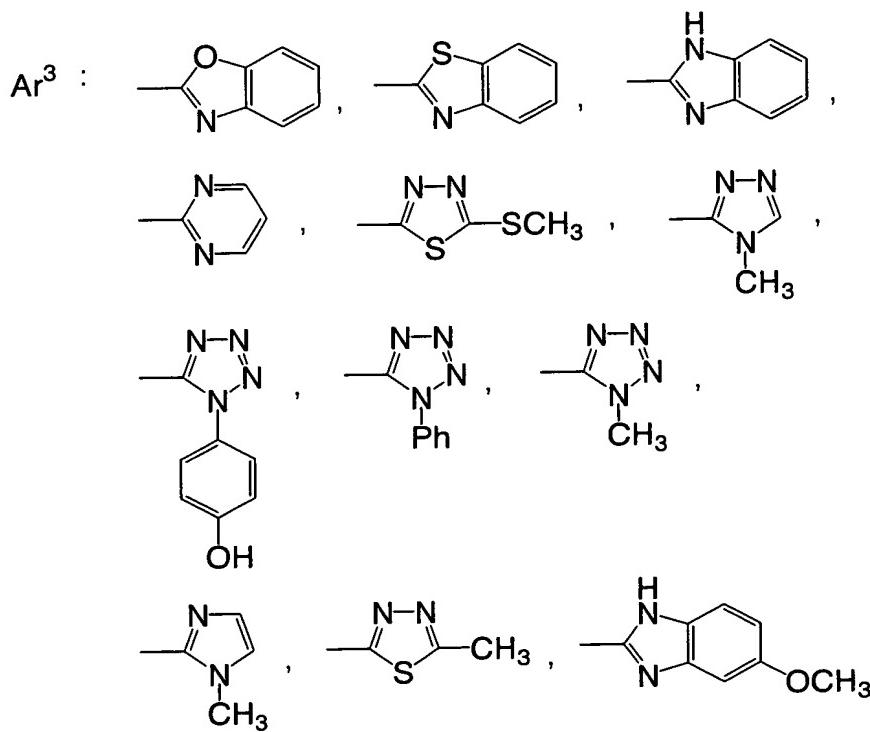


General formula (a<sup>+-</sup>3)

[0033]

In the general formula (a<sup>+-</sup>3), R<sup>1</sup> to R<sup>8</sup>, Ar<sup>1</sup>, Ar<sup>2</sup>, Y<sup>1</sup>, and Y<sup>2</sup> are respectively synonymous with those in the foregoing general formula (a<sup>+-</sup>2). Ar<sup>3</sup> represents an aromatic hydrocarbon group such as a phenyl group and a naphthyl group, or a monocyclic or polycyclic heterocyclic group containing at least one of nitrogen, oxygen and sulfur atoms, and preferably a heterocyclic group selected from the group consisting of thiazole based, benzothiazole based, naphthothiazole based, thianaphtheno-7,6,4,5-thiazole based, oxazole based, benzoxazole based, naphthoxazole based, selenazole based, benzoselenazole based, naphthoselenazole based, thiazoline based, 2-quinoline based, 4-quinoline based, 1-isoquinoline based, 3-isoquinoline based, benzoimidazole based, 3,3-dialkylbenzoindolenine based, 2-pyridine based, 4-pyridine based, 3,3-dialkylbenzo[e]indole based, tetrazole based, triazole based, pyrimidine based, and thiadiazole based groups. As the heterocyclic group, the following structures are the most preferable.

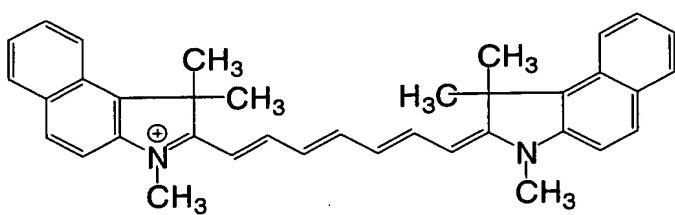
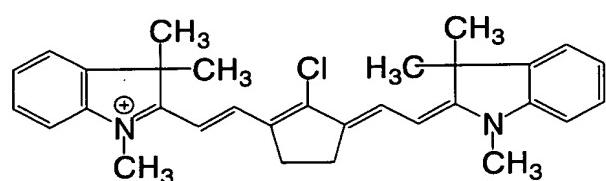
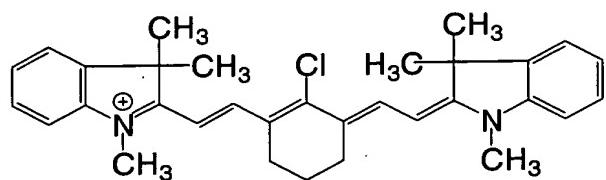
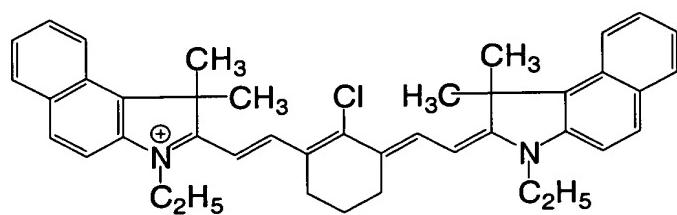
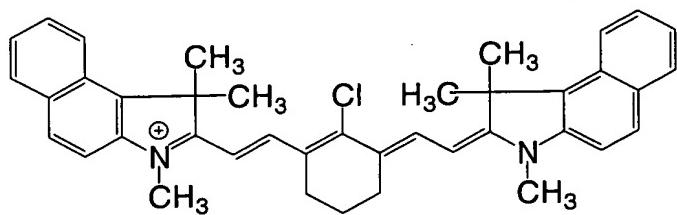
[0034]

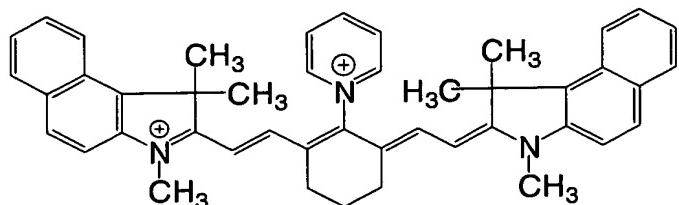
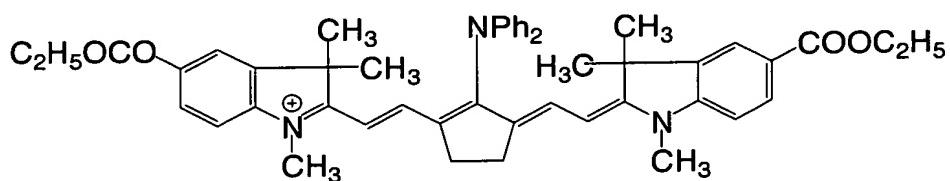
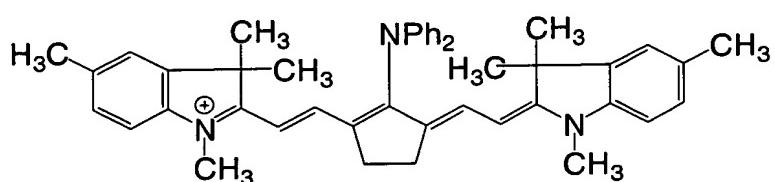
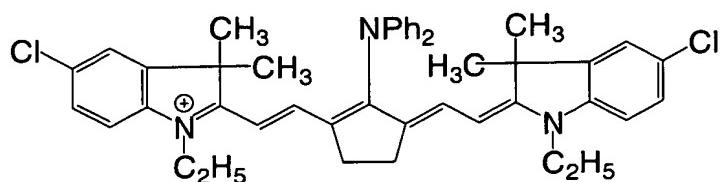
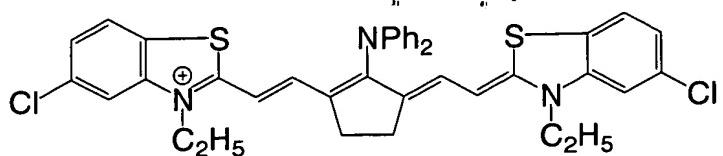


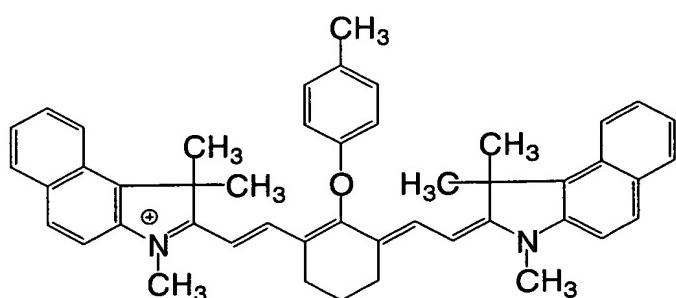
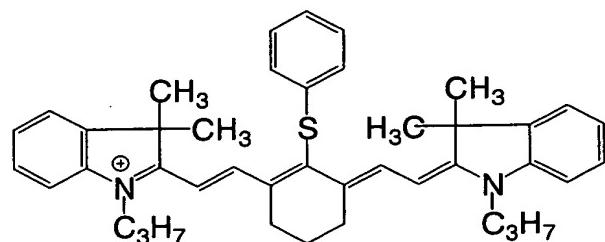
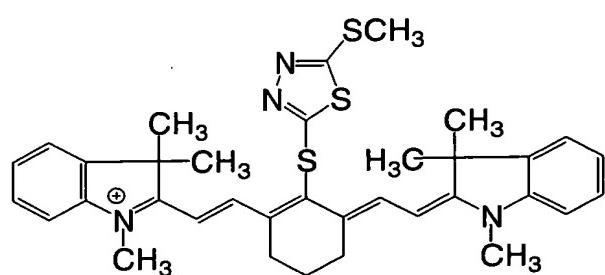
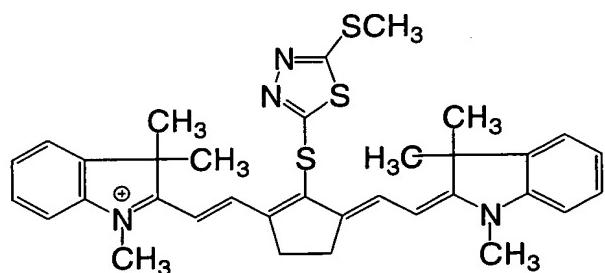
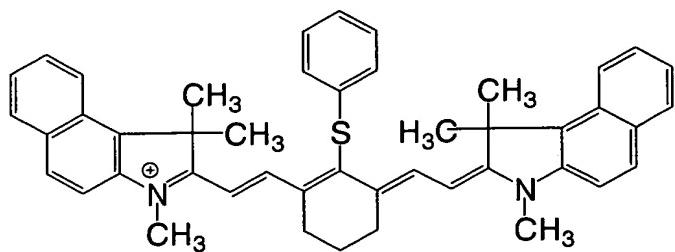
[0035]

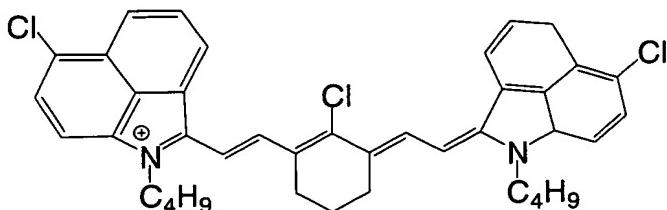
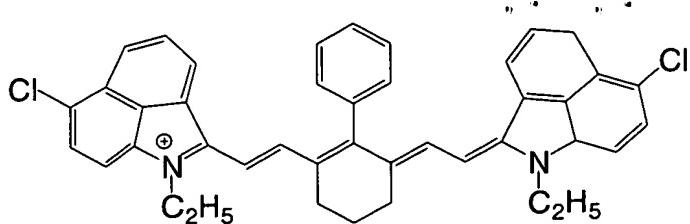
In the invention, specific examples of cation segments of the specific IR dye represented by the general formula ( $\text{a}^+$ ) that can suitably be used include cation segments of dyes described in paragraphs [0017] to [0019] of JP-A No. 2001-133969, paragraphs [0012] to [0038] of JP-A No. 2002-40638, and paragraphs [0012] to [0023] of JP-A No. 2002-23360, in addition to those enumerated below.

[0036]



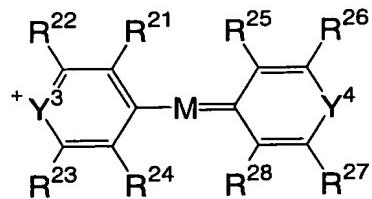






[0040]

General formula ( $c^+$ )



[0041]

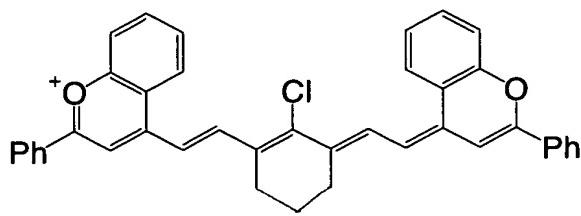
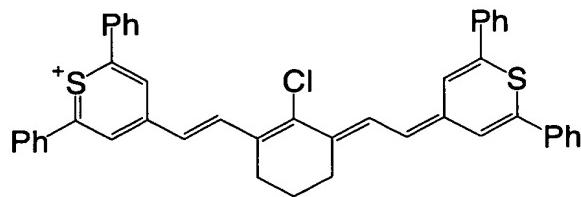
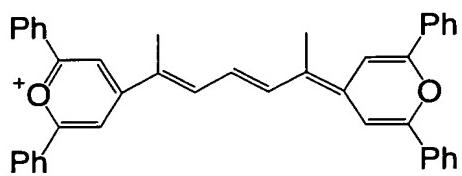
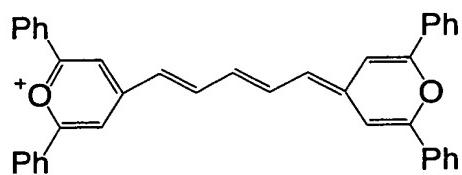
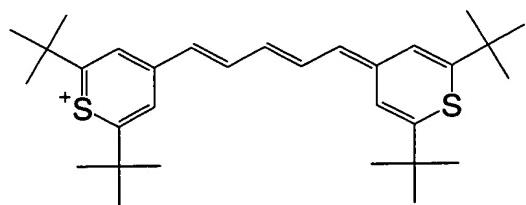
In the general formula ( $c^+$ ),  $\text{Y}^3$  and  $\text{Y}^4$  each independently represents an oxygen atom, a sulfur atom, a selenium atom, or a tellurium atom.  $\text{M}$  represents a methine chain having at least five or more conjugated carbon atoms.  $\text{R}^{21}$  to  $\text{R}^{24}$  and  $\text{R}^{25}$  to  $\text{R}^{28}$  each independently represents a hydrogen atom, a halogen atom, a cyano group, an alkyl group, an aryl group, an alkenyl group, an alkynyl group, a carbonyl group, a thio group, a sulfonyl group, a sulfinyl group, an oxy group, or an amino group.

[0042]

In the invention, specific examples of cation segments of

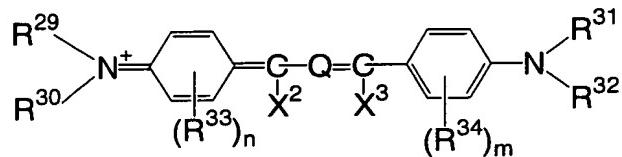
the specific IR dye represented by the general formula ( $c^+$ ) that can suitably be used include those enumerated below.

[0043]



[0044]

General formula (d<sup>+</sup>)



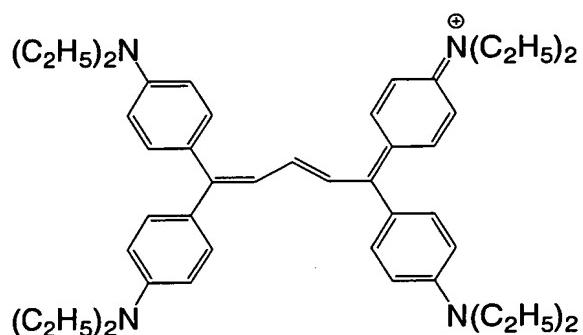
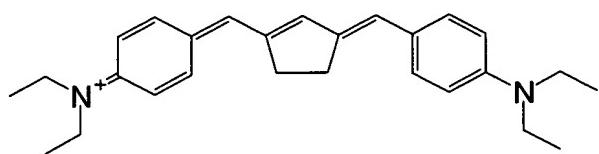
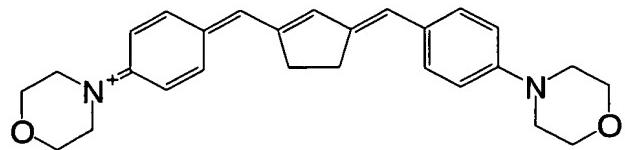
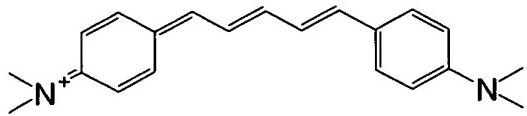
[0045]

In the general formula (d<sup>+</sup>), R<sup>29</sup> to R<sup>32</sup> each independently represents a hydrogen atom, an alkyl group, or an aryl group. R<sup>33</sup> and R<sup>34</sup> each independently represents an alkyl group, a substituted oxy group, or a halogen atom. n and m each independently represents an integer from 0 to 4. R<sup>29</sup> and R<sup>30</sup>, or R<sup>31</sup> and R<sup>32</sup> may bond with each other to form a ring, at least one of R<sup>29</sup> and R<sup>30</sup> may bond with R<sup>33</sup> to form a ring, and at least one of R<sup>31</sup> and R<sup>32</sup> may bond with R<sup>34</sup> to form a ring. Further, in the case when a plural number of R<sup>33</sup> or R<sup>34</sup> are present, the plurality of R<sup>33</sup> or the plurality of R<sup>34</sup> may bond with each other to form a ring. X<sup>2</sup> and X<sup>3</sup> each independently represents a hydrogen atom, an alkyl group, or an aryl group. Q represents an optionally substituted trimethine group or pentamethine group and may form a ring structure together with a divalent organic group.

[0046]

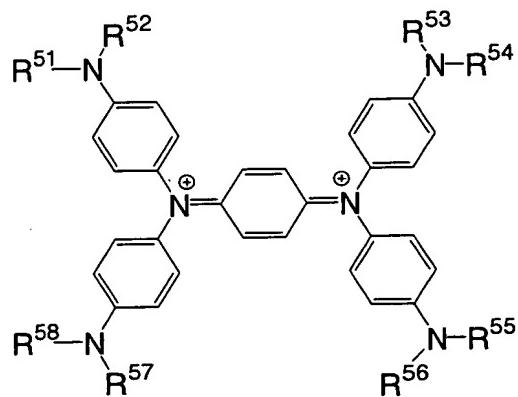
In the invention, specific examples of cation segments of the specific IR dye represented by the general formula (d<sup>+</sup>) that can suitably be used include those enumerated below.

[0047]

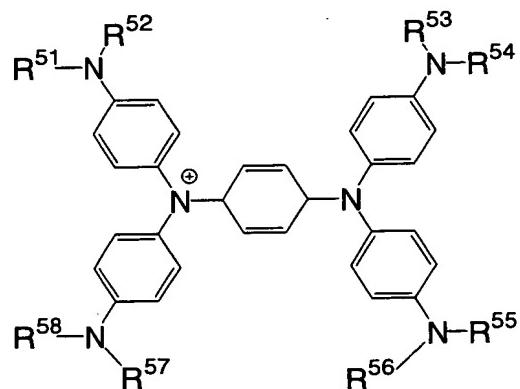


[0048]

General formula (f<sup>+</sup>-1)



General formula (f<sup>+</sup>-2)



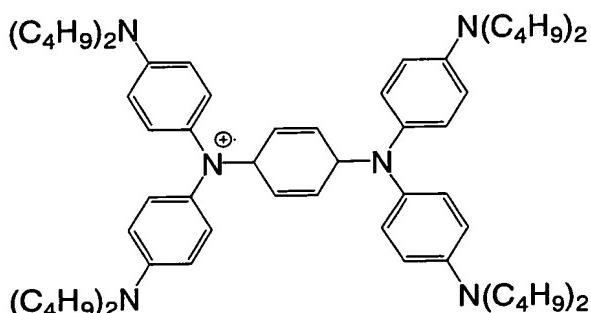
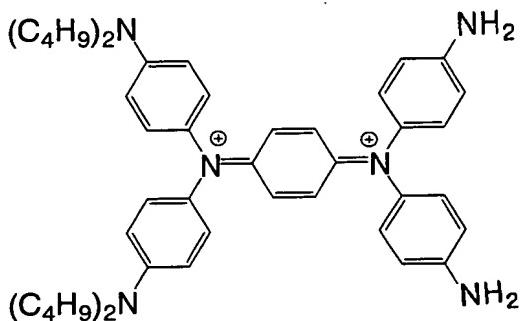
[0049]

In the general formulae (f<sup>+</sup>-1) and (f<sup>+</sup>-2), R<sup>51</sup> to R<sup>58</sup> each independently represents a hydrogen atom or an optionally substituted alkyl group or aryl group.

[0050]

In the present invention, specific examples of cation segments of the specific IR dye represented by the general formula (F-1) or (F-2) that can suitably be used include those enumerated below.

[0051]



[0052]

Of the specific IR absorbing materials represented by the general formula (1) according to the present invention, onium salts represented by the following general formula (1-A) can be enumerated as a preferred embodiment.

General formula (1-A):  $R^A-SO_3^-M^+$

In the general formula (1-A),  $R^A$  represents a substituent containing at least one substituent having an alkali-dissociating proton. Here, the substituent having an alkali-dissociating proton is synonymous with the substituent having an alkali-dissociating proton described above for the general formula (1).

$M^+$  is synonymous with  $M^+$  in the foregoing general formula (1).

[0053]

In  $R^A$ , as the skeleton to which the substituent having an alkali-dissociating proton is bonded, optionally substituted hydrocarbon groups can be enumerated, and those containing an aromatic ring in the structure thereof are preferable though they are not specifically limited. Examples of such aromatic rings include aromatic hydrocarbon rings such as a benzene ring, a naphthalene ring, an anthracene ring, and a phenanthrene ring and aromatic heterocyclic rings such as a pyrrole group, a pyridine ring, a quinoline ring, an acridine ring, an imidazole ring, a furan ring, a thiophene group, and a thiazole ring. Of these, aromatic hydrocarbon rings are preferable, and a benzene ring is the most preferable.

[0054]

Of the specific IR absorbing materials represented by the general formula (1), onium salts represented by the following general formula (1-B) can be enumerated as a more preferred embodiment.

General formula (1-B):  $Ar^B-SO_3^-M^+$

In the general formula (1-B),  $Ar^B$  represents an aryl group containing at least one substituent having an alkali-dissociating proton. Here, the substituent having an alkali-dissociating proton is synonymous with the substituent having an alkali-dissociating proton described above for the general formula (1).

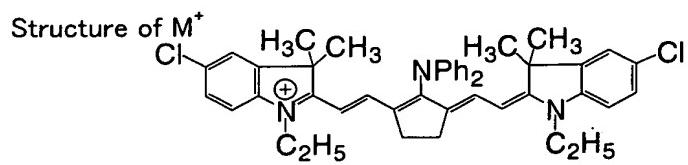
$M^+$  is synonymous with  $M^+$  in the foregoing general formula

(1).

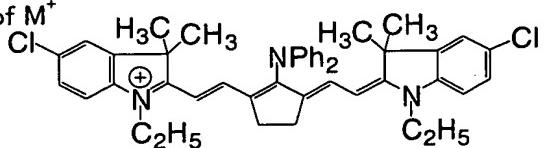
[0055]

Specific examples of the specific IR absorbing materials that are suitably used in the present invention will be given below. However, any of compounds represented by the general formula (1) can be arbitrarily selected within this range, and it should not be construed that the invention is limited to these illustrative compounds.

[0056]



Compound No.	Structure of $X^-$
CD-1	
CD-2	
CD-3	
CD-4	
CD-5	
CD-6	
CD-7	
CD-8	

Structure of  $M^+$ 

Compound No.	Structure of $X^-$
CD-9	<p>Structure of <math>X^-</math>: A benzene ring with a hydroxyl group (-OH) at the top position and a nitro group (-NO<sub>2</sub>) and a sulfonate group (-SO<sub>3</sub><sup>-</sup>) at the 4 and 5 positions respectively.</p>
CD-10	<p>Structure of <math>X^-</math>: A benzene ring with a chlorine atom (-Cl) at the top position, a hydroxyl group (-OH) at the 4-position, and two chlorine atoms (-Cl) at the 3 and 5 positions.</p>
CD-11	<p>Structure of <math>X^-</math>: A benzene ring with a carbonyl group (-C=O) at the top position, a hydroxyl group (-OH) at the 4-position, and a sulfonate group (-SO<sub>3</sub><sup>-</sup>) and a methoxy group (-OMe) at the 3 and 5 positions.</p>
CD-12	<p>Structure of <math>X^-</math>: A propyl chain ending in a sulfonate group (-CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub><sup>-</sup>).</p>
CD-13	<p>Structure of <math>X^-</math>: A benzene ring with a sulfonate group (-SO<sub>3</sub><sup>-</sup>) at the top position and a sulfonamido group (-SO<sub>2</sub>NHPh) at the 4-position.</p>
CD-14	<p>Structure of <math>X^-</math>: A propyl chain ending in a carboxylate group (-CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub><sup>-</sup>).</p>
CD-15	<p>Structure of <math>X^-</math>: A benzene ring with a hydroxyl group (-OH) at the top position, a carbonyl group (-C=O) at the 2-position, and a sulfonate group (-SO<sub>3</sub><sup>-</sup>) at the 4-position.</p>
CD-16	<p>Structure of <math>X^-</math>: A tricyclic system consisting of a quinone-like core with a carbonyl group (-C=O) at the 1-position, a hydroxyl group (-OH) at the 2-position, and a sulfonate group (-SO<sub>3</sub><sup>-</sup>) at the 4-position.</p>

Structure of  $M^+$

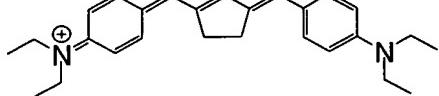


Compound No.	Structure of $X^-$
CD-17	A phenyl ring with a hydroxyl group (-OH) and a sulfonate group (-SO3^-).
CD-18	A phenyl ring with a carboxylic acid group (-COOH) and a sulfonate group (-SO3^-).
CD-19	A phenyl ring with a hydroxyl group (-OH) and a sulfonate group (-SO3^-).
CD-20	A phenyl ring with a carboxylic acid group (-COO-) and a sulfonate group (-SO3^-).
CD-21	A phenyl ring with a carboxylic acid group (-COOH) and a sulfonate group (-SO3^-).
CD-22	A phenyl ring with two carboxylic acid groups (-COOH) and a sulfonate group (-SO3^-).
CD-23	A phenyl ring with a hydroxyl group (-OH) and a sulfonate group (-SO3^-).
CD-24	A phenyl ring with a hydroxyl group (-OH), a carboxylic acid group (-COOH), and a sulfonate group (-SO3^-).

Structure of  $M^+$ 

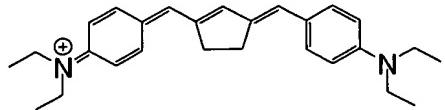
Compound No.	Structure of $X^-$
CD-25	
CD-26	
CD-27	
CD-28	
CD-29	
CD-30	
CD-31	
CD-32	

Structure of  $M^+$ :



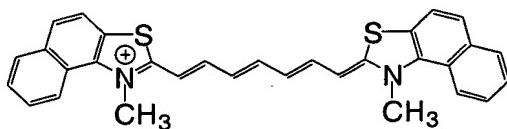
Compound No.	Structure of $X^-$
CD-33	<p>Phenoxide anion (<math>X^-</math>): A benzene ring with a hydroxyl group (<math>\text{OH}</math>) and a sulfonate group (<math>\text{SO}_3^-</math>).</p>
CD-34	<p>4-sulfophenyl carboxylic acid anion (<math>X^-</math>): A benzene ring with a carboxylic acid group (<math>\text{COOH}</math>) and a sulfonate group (<math>\text{SO}_3^-</math>).</p>
CD-35	<p>4-hydroxyphenyl sulfonate anion (<math>X^-</math>): A benzene ring with a hydroxyl group (<math>\text{OH}</math>) and a sulfonate group (<math>\text{SO}_3^-</math>).</p>
CD-36	<p>4-sulfophenyl dicarboxylic acid anion (<math>X^-</math>): A benzene ring with two carboxylic acid groups (<math>\text{HOOC COOH}</math>) and a sulfonate group (<math>\text{SO}_3^-</math>).</p>
CD-37	<p>4-sulfophenyl tricarboxylic acid anion (<math>X^-</math>): A benzene ring with three carboxylic acid groups (<math>\text{HOOC COOH COOH}</math>) and a sulfonate group (<math>\text{SO}_3^-</math>).</p>
CD-38	<p>4-sulfophenyl tetracarboxylic acid anion (<math>X^-</math>): A benzene ring with four carboxylic acid groups (<math>\text{HOOC COOH COOH COOH}</math>) and a sulfonate group (<math>\text{SO}_3^-</math>).</p>
CD-39	<p>2-hydroxyphenyl sulfonate anion (<math>X^-</math>): A benzene ring with a hydroxyl group (<math>\text{OH}</math>) at position 2 and a sulfonate group (<math>\text{SO}_3^-</math>).</p>
CD-40	<p>2-hydroxyphenyl tricarboxylic acid anion (<math>X^-</math>): A benzene ring with a hydroxyl group (<math>\text{OH}</math>) at position 2 and three carboxylic acid groups (<math>\text{COOH COOH COOH}</math>) at positions 1, 3, and 5, and a sulfonate group (<math>\text{SO}_3^-</math>).</p>

Structure of  $M^+$ :



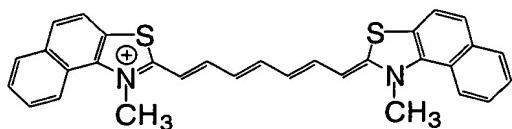
Compound No.	Structure of $X^-$
CD-41	<p>The structure is a 4-nitrophenoxide anion (<math>\text{C}_6\text{H}_4\text{NO}_2\text{O}^-</math>) with a sulfonate group (<math>\text{SO}_3^-</math>) at the para position.</p>
CD-42	<p>The structure is a 2,6-dichlorophenoxide anion (<math>\text{C}_6\text{H}_3\text{Cl}_2\text{O}^-</math>) with a sulfonate group (<math>\text{SO}_3^-</math>) at the para position.</p>
CD-43	<p>The structure is a 2-hydroxy-4-methoxyphenoxide anion (<math>\text{C}_6\text{H}_4\text{CO}_2\text{O}^-</math>) with a methoxy group (<math>\text{OMe}</math>) and a sulfonate group (<math>\text{SO}_3^-</math>) at the para position.</p>
CD-44	<p>The structure is a 3-sulfopropyl sulfonate anion (<math>\text{HS}(\text{CH}_2)_2\text{SO}_3^-</math>).</p>
CD-45	<p>The structure is a 4-(N-phenylsulfonamido)phenoxide anion (<math>\text{C}_6\text{H}_4\text{SO}_2\text{NHPhO}^-</math>).</p>
CD-46	<p>The structure is a 3-sulfopropyl carboxylate anion (<math>\text{HO}_2\text{C}(\text{CH}_2)_2\text{SO}_3^-</math>).</p>
CD-47	<p>The structure is a 4-(2-sulfopropyl)phenoxide anion (<math>\text{C}_6\text{H}_4\text{CO}_2\text{N}(\text{CH}_2\text{CH}_2\text{SO}_3^-)\text{H}</math>).</p>
CD-48	<p>The structure is a 2-hydroxy-4,6-dihydroxyphenoxide anion (<math>\text{C}_6\text{H}_3(\text{OH})_2\text{O}_2^-</math>) with a sulfonate group (<math>\text{SO}_3^-</math>) at the para position.</p>

Structure of  $M^+$ :



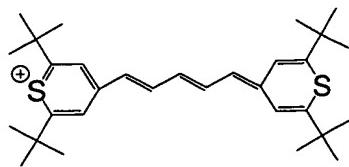
Compound No.	Structure of $X^-$
CD-49	$\text{OH}$ $\text{SO}_3^-$
CD-50	$\text{COOH}$ $\text{SO}_3^-$
CD-51	$\text{HO}$ $\text{SO}_3^-$
CD-52	$\text{HOOC}$ $\text{SO}_3^-$
CD-53	$\text{COOH}$ $\text{SO}_3^-$
CD-54	$\text{HOOC-COOH}$ $\text{SO}_3^-$
CD-55	$\text{OH}$ $\text{SO}_3^-$
CD-56	$\text{OH-COOH}$ $\text{SO}_3^-$

Structure of  $M^+$ :



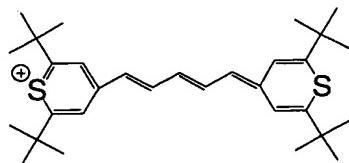
Compound No.	Structure of $X^-$
CD-57	
CD-58	
CD-59	
CD-60	
CD-61	
CD-62	
CD-63	
CD-64	

Structure of  $M^+$ :



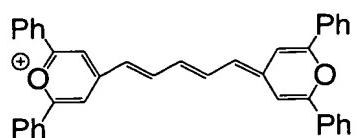
Compound No.	Structure of $X^-$
PD-1	<p>Phenoxide anion (<math>\text{C}_6\text{H}_4\text{O}^-</math>) with a sulfonate group (<math>\text{SO}_3^-</math>) attached at the para position.</p>
PD-2	<p>Phenyl sulfonate anion (<math>\text{C}_6\text{H}_4\text{SO}_3^-</math>) with a carboxylic acid group (<math>\text{COOH}</math>) attached at the para position.</p>
PD-3	<p>4-hydroxyphenyl sulfonate anion (<math>\text{HO-C}_6\text{H}_3\text{SO}_3^-</math>) with a carboxylic acid group (<math>\text{COOH}</math>) attached at the para position.</p>
PD-4	<p>4-carboxyphenyl sulfonate anion (<math>\text{HOOC-C}_6\text{H}_3\text{SO}_3^-</math>) with a carboxylic acid group (<math>\text{COOH}</math>) attached at the para position.</p>
PD-5	<p>3,4-dicarboxyphenyl sulfonate anion (<math>\text{HOOC-C}_6\text{H}_2\text{COOH-SO}_3^-</math>) with a carboxylic acid group (<math>\text{COOH}</math>) attached at the para position.</p>
PD-6	<p>2-hydroxyphenyl sulfonate anion (<math>\text{HO-C}_6\text{H}_3\text{SO}_3^-</math>) with a carboxylic acid group (<math>\text{COOH}</math>) attached at the para position.</p>
PD-7	<p>2,6-dihydrophenyl sulfonate anion (<math>\text{HO-C}_6\text{H}_3\text{SO}_3^-</math>) with a carboxylic acid group (<math>\text{COOH}</math>) attached at the para position.</p>
PD-8	<p>2-hydroxyphenyl sulfonate anion (<math>\text{HO-C}_6\text{H}_3\text{SO}_3^-</math>) with a carboxylic acid group (<math>\text{COOH}</math>) attached at the para position.</p>

Structure of  $M^+$ :



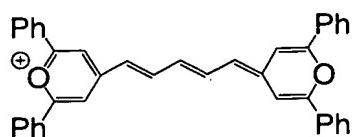
Compound No.	Structure of $X^-$
PD-9	<p>The anion consists of a benzene ring with a hydroxyl group (-OH) at position 1 and a nitro group (-NO<sub>2</sub>) at position 4. At position 2, there is a sulfonate group (-SO<sub>3</sub><sup>-</sup>).</p>
PD-10	<p>The anion consists of a benzene ring with a chlorine atom (-Cl) at position 1, a hydroxyl group (-OH) at position 2, and another chlorine atom (-Cl) at position 3. At position 4, there is a sulfonate group (-SO<sub>3</sub><sup>-</sup>).</p>
PD-11	<p>The anion consists of a benzene ring with a phenyl group (-Ph) at position 1, a carbonyl group (-C=O) at position 2, a hydroxyl group (-OH) at position 3, and a methoxy group (-OMe) at position 4. At position 5, there is a sulfonate group (-SO<sub>3</sub><sup>-</sup>).</p>
PD-12	<p>The anion consists of a three-carbon chain ending in a sulfonate group (-HS-CH<sub>2</sub>-CH<sub>2</sub>-SO<sub>3</sub><sup>-</sup>).</p>
PD-13	<p>The anion consists of a benzene ring with a phenylsulfone group (-Ph-SO<sub>2</sub>-NHPh) at position 1 and a sulfonate group (-SO<sub>3</sub><sup>-</sup>) at position 2.</p>
PD-14	<p>The anion consists of a two-carbon chain ending in a sulfonate group (-HO<sub>2</sub>C-CH<sub>2</sub>-SO<sub>3</sub><sup>-</sup>).</p>
PD-15	<p>The anion consists of a benzene ring with a hydroxyl group (-OH) at position 1, a carbonyl group (-C=O) at position 2, and a sulfonate group (-SO<sub>3</sub><sup>-</sup>) at position 3. A hydrogen atom is shown above the carbonyl group.</p>
PD-16	<p>The anion consists of a tricyclic system: a quinone-like core with a carbonyl group (-C=O) at position 1, a hydroxyl group (-OH) at position 2, and another hydroxyl group (-OH) at position 3. At position 4, there is a sulfonate group (-SO<sub>3</sub><sup>-</sup>).</p>

Structure of  $M^+$ :



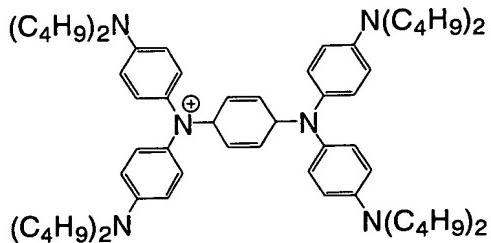
Compound No.	Structure of $X^-$
PD-17	<p>Chemical structure of PD-17: A benzene ring with a hydroxyl group (-OH) and a sulfonate group (-SO<sub>3</sub><sup>-</sup>) attached.</p>
PD-18	<p>Chemical structure of PD-18: A benzene ring with a carboxylic acid group (-COOH) and a sulfonate group (-SO<sub>3</sub><sup>-</sup>) attached.</p>
PD-19	<p>Chemical structure of PD-19: A benzene ring with a hydroxyl group (-OH) at the 3-position and a sulfonate group (-SO<sub>3</sub><sup>-</sup>) attached.</p>
PD-20	<p>Chemical structure of PD-20: A benzene ring with a carboxylic acid group (-COOH) at the 3-position and a sulfonate group (-SO<sub>3</sub><sup>-</sup>) attached.</p>
PD-21	<p>Chemical structure of PD-21: A benzene ring with a carboxylic acid group (-COOH) and a sulfonate group (-SO<sub>3</sub><sup>-</sup>) attached, which is part of a dianion where the sulfonate group is shared with another benzene ring.</p>
PD-22	<p>Chemical structure of PD-22: A benzene ring with carboxylic acid groups (-COOH) at the 3 and 4 positions and a sulfonate group (-SO<sub>3</sub><sup>-</sup>) attached.</p>
PD-23	<p>Chemical structure of PD-23: A naphthalene ring with a hydroxyl group (-OH) at the 2-position and a sulfonate group (-SO<sub>3</sub><sup>-</sup>) attached.</p>
PD-24	<p>Chemical structure of PD-24: A benzene ring with a hydroxyl group (-OH) at the 2-position, a carboxylic acid group (-COOH) at the 3-position, and a sulfonate group (-SO<sub>3</sub><sup>-</sup>) attached.</p>

### Structure of $M^+$ :



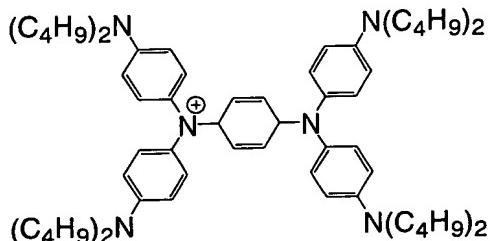
Compound No.	Structure of X <sup>-</sup>
PD-25	
PD-26	
PD-27	
PD-28	
PD-29	
PD-30	
PD-31	
PD-32	

Structure of  $M^+$ :



Compound No.	Structure of $X^-$
AD-1	
AD-2	
AD-3	
AD-4	
AD-5	
AD-6	
AD-7	
AD-8	

Structure of  $M^+$ :



Compound No.	Structure of $X^-$
AD-9	
AD-10	
AD-11	
AD-12	
AD-13	
AD-14	
AD-15	
AD-16	

[0070]

The specific IR absorbing material that is used in the image forming material of the present invention may be used singly or in admixture of two or more thereof. The content of the specific IR absorbing material is preferably not more than 50 % of the mass of

the whole of solid contents of the image forming layer from the viewpoint of film forming property; preferably in the range of 0.1 % to 30 % from the viewpoint that the image forming property is extremely good; and most preferably in the range of 0.5 % to 15 % from the viewpoint that the printing performance such as press life can consist with the image forming property at high levels.

[0071]

[(A) Water-insoluble and alkali-soluble high-molecular compound]

The water-insoluble and alkali-soluble high-molecular compound (alkali-soluble resin) (A) that can be used in the positive image forming layer in the present invention includes homopolymers having an acid group in the main chain or side chains thereof and copolymers or mixtures thereof. The acid group may be introduced by any of a method of introducing it by polymerizing a monomer previously having an acid group and a method of introducing it by polymeric reaction after polymerization, or a combination of these methods.

[0072]

Examples of such alkali-soluble resins include phenol resins described in Phenol Resins, published by Plastic Age Co., Ltd., Synthesis, Curing, Toughening and Application of Phenol Resins, published by IPC Ltd., Plastic Material Course (15): Phenol Resins, published by The Nikkan Kogyo Shimbun, Ltd., and Plastic Book (15): Phenol Resins, published by Kogyo Chosakai Publishing Co., Ltd.; polyhydroxystyrenes; polyhalogenated

hydroxystyrenes; N-(4-hydroxyphenyl)methacrylamide copolymers; hydroquinone monomethacrylate copolymers; sulfonylimide based polymers described in JP-A No. 7-28244; carboxyl group-containing polymers described in JP-A No. 7-36184; phenolic hydroxyl group-containing acrylic resins described in JP-A No. 51-34711; sulfonamide group-containing acrylic resins described in JP-A No. 2-866; urethane based resins; and various alkali-soluble high-molecular compounds. Though there are no particular limitations with respect to the alkali-soluble resin, ones having an acid group selected from the following (1) to (6) groups in the main chain or side chains thereof are preferable from the standpoints of solubility in alkaline developing solutions and revelation of dissolution inhibiting ability.

[0073]

- (1) Phenol group (-Ar-OH)
- (2) Sulfonamide group (-SO<sub>2</sub>NH-R)
- (3) Substituted sulfonamide based acid group (hereinafter referred to as "active imide group") [-SO<sub>2</sub>NHCOR, -SO<sub>2</sub>NHSO<sub>2</sub>R, and -CONHSO<sub>2</sub>R]
- (4) Carboxylic acid group (-CO<sub>2</sub>H)
- (5) Sulfonic acid group (-SO<sub>3</sub>H)
- (6) Phosphoric acid group (-OPO<sub>3</sub>H<sub>2</sub>)

[0074]

In the foregoing (1) to (6) groups, Ar represents an

optionally substituted divalent aryl connecting group; and R represents an optionally substituted hydrocarbon group.

[0075]

Of the alkali-soluble resins having an acid group selected from the foregoing (1) to (6) groups, are preferable alkali-soluble resins having (1) a phenol group, (2) a sulfonamide group, (3) an active imide group, or (4) a carboxylic acid group. Especially, alkali-soluble resins having (1) a phenol group, (2) a sulfonamide group, or (4) a carboxylic acid group are the most preferable from the standpoint of sufficiently ensuring solubility in alkaline developing solutions, development latitude and film strength.

[0076]

As the alkali-soluble resin having an acid group selected from the foregoing (1) to (6) groups, can be enumerated the following resins.

Examples of alkali-soluble resins having (1) a phenol group include novolac resins, resol resins, polyvinylphenol resins, and phenolic hydroxyl group-containing acrylic resins. From the viewpoints of image forming property and thermosetting property, novolac resins, resol resins, and polyvinylphenol resins are preferable; from the viewpoint of stability, novolac resins and polyvinylphenol resins are more preferable; and from the viewpoints of easiness of availability of raw materials and flexibility of raw materials, novolac resins are particularly preferable.

[0077]

The novolac resins as referred to herein mean resins obtained by polycondensing at least one kind of phenols such as phenol, o-cresol, m-cresol, p-cresol, 2,5-xylenol, 3,5-xylenol, o-ethylphenol, m-ethylphenol, p-ethylphenol, propylphenol, n-butylphenol, tert-butylphenol, 1-naphthol, 2-naphthol, pyrrocatechol, resorsinol, hydroquinone, pyrogallol, 1,2,4-benzenetriol, fluoroglucinol, 4,4'-biphenyldiol, and 2,2-bis(4'-hydroxyphenyl)propane with at least one kind of aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, benzaldehyde, and furfural (paraformaldehyde and paraldehyde may be used in place of formaldehyde and acetaldehyde, respectively) or ketones such as acetone, methyl ethyl ketone, and methyl isobutyl ketone in the presence of an acid catalyst.

[0078]

In the present invention, polycondensates of phenol, o-cresol, m-cresol, p-cresol, 2,5-xylenol, 3,5-xylenol, or resorcinol as the phenol with formaldehyde, acetaldehyde, or propionaldehyde as the aldehyde or ketone are preferable. Especially, polycondensates of a mixed phenol of m-cresol, p-cresol, 2,5-xylenol, 3,5-xylenol and resorcinol in a mixing molar ratio of (40 to 100) to (0 to 50) to (0 to 20) to (0 to 20) to (0 to 20) or a mixed phenol of phenol, m-cresol and p-cresol in a mixing molar ratio of (0 to 100) to (0 to 70) to (0 to 60) with formaldehyde are preferable.

[0079]

Incidentally, it is preferred that the positive image forming layer in the invention contains a solvent inhibitor. In such a case, polycondensates of a mixed phenol of m-cresol, p-cresol, 2,5-xylenol, 3,5-xylenol and resorcinol in a mixing molar ratio of (70 to 100) to (0 to 30) to (0 to 20) to (0 to 20) to (0 to 20) or a mixed phenol of phenol, m-cresol and p-cresol in a mixing molar ratio of (10 to 100) to (0 to 60) to (0 to 40) with formaldehyde are preferable.

[0080]

Examples of phenol group-containing alkali-soluble resins include polymers of phenol group-containing polymerizable monomers.

Examples of phenol group-containing polymerizable monomers include phenol group-containing acrylamides, methacrylamides, acrylic acid esters, methacrylic acid esters, and hydroxystyrenes.

Specific examples of phenol group-containing polymerizable monomers that can suitably be used include N-(2-hydroxyphenyl)acrylamide, N-(3-hydroxyphenyl)acrylamide, N-(4-hydroxyphenyl)acrylamide, N-(2-hydroxyphenyl)-methacrylamide, N-(3-hydroxyphenyl)methacrylamide, N-(4-hydroxyphenyl)methacrylamide, o-hydroxyphenyl acrylate, m-hydroxyphenyl acrylate, p-hydroxyphenyl acrylate, o-hydroxyphenyl methacrylate, m-hydroxyphenyl methacrylate,

p-hydroxyphenyl methacrylate, o-hydroxystyrene, m-hydroxystyrene, p-hydroxystyrene, 2-(2-hydroxyphenyl)ethyl acrylate, 2-(3-hydroxyphenyl)ethyl acrylate, 2-(4-hydroxyphenyl)ethyl acrylate, 2-(2-hydroxyphenyl)ethyl methacrylate, 2-(3-hydroxyphenyl)ethyl methacrylate, and 2-(4-hydroxyphenyl)ethyl methacrylate.

[0081]

Further, an acid group may be derived by polymerization of an acid group precursor and then polymeric reaction. For example, after polymerizing p-acetoxystyrene as an acid group precursor, the ester segment may be derived into a phenolic hydroxyl group upon hydrolysis. Moreover, polycondensates of a phenol containing an alkyl group having from 3 to 8 carbon atoms as a substituent with formaldehyde, such as t-butyl-phenol-formaldehyde resins and octylphenol-formaldehyde resins, as described in USP No. 4,123,279, can be enumerated as preferred examples.

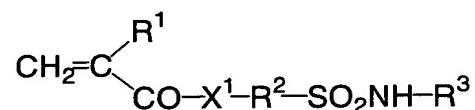
[0082]

Examples of alkali-soluble resins having (2) a sulfonamide group include polymers constituted of a minimum constituent unit derived from a sulfonamide group-containing compound as the major constituent component. As such a compound are enumerated compounds having one or more sulfonamide groups having at least one hydrogen atom bonded to a nitrogen atom and one or more polymerizable unsaturated groups within the

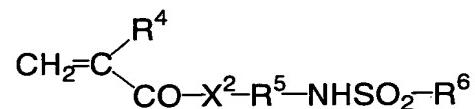
molecule thereof. Especially, low-molecular compounds having an acryloyl group, an allyl group or a vinyloxy group and a substituted or monosubstituted aminosulfonyl group or a substituted sulfonylimino group within the molecule thereof are preferable, and examples include compounds represented by the following general formulae (i) to (v).

[0083]

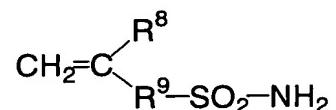
General formula (i)



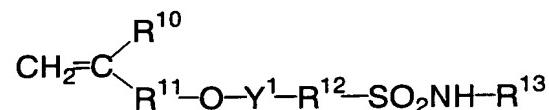
General formula (ii)



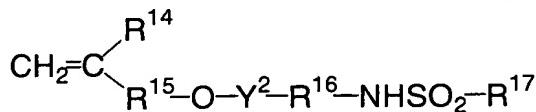
General formula (iii)



General formula (iv)



General formula (v)



[0084]

In the general formulae (i) to (v),  $\text{X}^1$  and  $\text{X}^2$  each independently represents  $-\text{O}-$  or  $-\text{NR}^7$ .  $\text{R}^1$  and  $\text{R}^4$  each independently represents a hydrogen atom or  $-\text{CH}_3$ .  $\text{R}^2$ ,  $\text{R}^5$ ,  $\text{R}^9$ ,  $\text{R}^{12}$  and  $\text{R}^{16}$  each independently represents an optionally substituted alkylene group having from 1 to 12 carbon atoms, cycloalkylene group, arylene group or aralkylene group.  $\text{R}^3$ ,  $\text{R}^7$  and  $\text{R}^{13}$  each independently represents a hydrogen atom or an optionally substituted alkyl group having from 1 to 12 carbon atoms, cycloalkyl group, aryl group or aralkyl group.  $\text{R}^6$  and  $\text{R}^{17}$  each independently represents an optionally substituted alkyl group having from 1 to 12 carbon atoms, cycloalkyl group, aryl group or aralkyl group.  $\text{R}^8$ ,  $\text{R}^{10}$  and  $\text{R}^{14}$  each independently represents a hydrogen atom or  $-\text{CH}_3$ .  $\text{R}^{11}$  and  $\text{R}^{15}$  each independently represents a single bond or an optionally substituted alkylene group having from 1 to 12 carbon atoms, cycloalkylene group, arylene group or aralkylene group.  $\text{Y}^1$  and  $\text{Y}^2$  each independently represents a single bond or CO.

[0085]

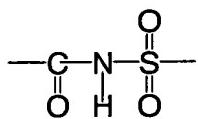
Of the compounds represented by the general formulae (i) to (v), in particular, m-aminosulfonylphenyl methacrylate, N-(p-aminosulfonylphenyl)methacrylamide, and N-(p-amino-

sulfonylphenyl)acrylamide can suitably be used in the invention.

[0086]

Examples of alkali-soluble resins having (3) an active imide group include polymers constituted of a minimum constituent unit derived from an active imide group-containing compound as the major constituent component. As such a compound are enumerated compounds having one or more active imide groups represented by the following structural formula and one or more polymerizable unsaturated groups within the molecule thereof.

[0087]



[0088]

Specifically, N-(p-toluenesulfonyl)methacrylamide and N-(p-toluenesulfonyl)acrylamide can suitably be used.

[0089]

Examples of alkali-soluble resins having (4) a carboxylic acid group include polymers constituted of a minimum constituent unit derived from a compound having one or more carboxylic acid groups and one or more polymerizable unsaturated groups within the molecule thereof as the major constituent component.

[0090]

Examples of alkali-soluble resins having (5) a sulfonic acid group include polymers constituted of a minimum constituent unit derived from a compound having one or more sulfonic acid groups and one or more polymerizable unsaturated groups within the molecule thereof as the major constituent component.

[0091]

Examples of alkali-soluble resins having (6) a phosphoric acid group include polymers constituted of a minimum constituent unit derived from a compound having one or more phosphoric acid groups and one or more polymerizable unsaturated groups within the molecule thereof as the major constituent component.

[0092]

The minimum constituent component unit having an acid group selected from the foregoing (1) to (6) groups, which constitutes the alkali-soluble resin to be used in the positive image forming layer is not always limited to one kind only. Copolymers of two kinds or more minimum constituent units having the same acid group or two kinds or more minimum constituent units each having a different acid group can also be used.

[0093]

The copolymers containing 10 % by mole or more, and preferably 20 % by mole or more of a compound having an acid group selected from the foregoing (1) to (6) groups, which is to be

copolymerized, are preferable. When the copolymers contain the above compound in the amount less than 10 % by mole, alkali solubility may be insufficient and enhancement of solubility discrimination may not sufficiently achieved.

[0094]

In the present invention, in the case where a compound is copolymerized, and an alkali-soluble resin is used as a copolymer, other compounds not containing an acid group selected from the foregoing (1) to (6) groups can be used as the compound to be copolymerized. As other compounds not containing an acid group selected from the foregoing (1) to (6) groups, compounds set forth in the following (m1) to (m13) groups can be enumerated, but it should not be construed that the invention is limited thereto.

[0095]

(m1) Acrylic acid esters and methacrylic acid esters having an aliphatic hydroxyl group, such as 2-hydroxyethyl acrylate and 2-hydroxyethyl methacrylate.

(m2) Alkyl acrylates such as methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, amyl acrylate, hexyl acrylate, octyl acrylate, benzyl acrylate, 2-chloroethyl acrylate, and glycidyl acrylate.

(m3) Alkyl methacrylates such as methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, amyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, 2-chloroethyl methacrylate, and glycidyl

methacrylate.

(m4) Acrylamides and methacrylamides such as acrylamide, methacrylamide, N-methylolacrylamide, N-ethylacrylamide, N-hexylmethacrylamide, N-cyclohexylacrylamide, N-hydroxyethylacrylamide, N-phenylacrylamide, N-nitrophenylacrylamide, and N-ethyl-N-phenylacrylamide.

[0096]

(m5) Vinyl ethers such as ethyl vinyl ether, 2-chloroethyl vinyl ether, hydroxyethyl vinyl ether, propyl vinyl ether, butyl vinyl ether, octyl vinyl ether, and phenyl vinyl ether.

(m6) Vinyl esters such as vinyl acetate, vinyl chloroacetate, vinyl butyrate, and vinyl benzoate.

(m7) Styrenes such as styrene,  $\alpha$ -methylstyrene, methylstyrene, chloromethylstyrene, and p-acetoxystyrene.

(m8) Vinyl ketones such as methyl vinyl ketone, ethyl vinyl ketone, propyl vinyl ketone, and phenyl vinyl ketone.

(m9) Olefins such as ethylene, propylene, isobutylene, butadiene, and isoprene.

[0097]

(m10) N-Vinylpyrrolidone, acrylonitrile, methacrylonitrile, and the like.

(m11) Unsaturated imides such as maleimide, N-acryloylacrylamide, N-acetylmethacrylamide, N-propionylmethacrylamide, and N-(p-chlorobenzoyl)methacrylamide.

(m12) Maleic anhydride, itaconic anhydride, acrylic acid chloride, methacrylic acid chloride, and the like.

(m13) Methacrylic acid based monomers having a hetero atom bonded at the  $\alpha$ -position, such as compounds described in Japanese Patent Application Nos. 2001-115595 and 2001-115598.

[0098]

In the present invention, in the case where the alkali-soluble resin is a homopolymer or copolymer of a polymerizable monomer having (1) a phenolic hydroxyl group, a polymerizable monomer having (2) a sulfonamide group, a polymerizable monomer having (3) an active imide group, a polymerizable monomer having (4) a carboxylic acid group, a polymerizable monomer having (5) a sulfonic acid group, or a polymerizable monomer having (6) a phosphoric acid group, ones having a weight average molecular weight as reduced into polystyrene by the gel permeation chromatography method (hereinafter simply referred to as "weight average molecular weight") of 2,000 or more and a number average molecular weight of 500 or more are preferable, and ones having a weight average molecular weight from 5,000 to 300,000 and a number average molecular weight from 800 to 250,000, with a degree of dispersion (weight average molecular weight/number average molecular weight) being from 1.1 to 10, are more preferable.

[0099]

In the present invention, in the case where the alkali-soluble high-molecular compound is a novolac resin, ones having a weight average molecular weight from 500 to 100,000 and a number average molecular weight from 200 to 50,000 are preferable. Novolac resins having a low ratio of low-molecular component described in Japanese Patent Application No. 2001-126278 may also be used.

[0100]

The alkali-soluble resins may be used singly or in combination of two or more thereof and are used in an addition amount from 30 to 99 % by mass, preferably from 40 to 95 % by mass, and particularly preferably from 50 to 90 % by mass in the whole of solid contents of the image forming layer (photosensitive layer). When the total addition amount of the alkali-soluble resin is less than 30 % by mass, durability of the photosensitive layer is deteriorated. On the other hand, the addition amount exceeding 99 % by mass is not preferred from the viewpoints of sensitivity and image forming property.

[0101]

In the case where a combination of alkali-soluble resins is used, any combinations can be used. Examples of particularly preferred combinations include a combination of a phenolic hydroxyl group-containing polymer and a sulfonamide group-containing polymer, a combination of a phenolic hydroxyl group-containing polymer and a carboxylic acid group-containing

polymer, a combination of two kinds or more of phenolic hydroxyl group-containing polymers, and combinations with polycondensates of phenol and formaldehyde containing an alkyl group having from 3 to 8 carbon atom as a substituent, such as a polycondensate of t-butylphenol and formaldehyde and a polycondensate of octylphenol and formaldehyde, as described in USP No. 4,123,279, and alkaline-soluble resins having an electron-withdrawing group-containing phenol structure on the aromatic ring, as described in JP-A No. 2000-241972.

[0102]

**[(C) Light-heat Converting agent]**

In the present invention, the following light-heat converting agent (C) may be used in combination with the specific IR coloring material according to the invention, the use of which is, however, not essential.

As the light-heat converting agent (C) to be used in the present invention, any substances that absorb light energy radiations used for recording to generate a heat can be used without limitations on absorption wavelength region. However, infrared absorbing dyes or pigments having an absorption maximum at a wavelength of 760 nm to 1,200 nm are preferable from the viewpoint of adaptability to readily available high-output lasers.

[0103]

**(Infrared absorbing dye or pigment)**

As dyes, commercially available dyes and known dyes described in literatures such as Dye Handbooks (edited by The Society of Synthetic Organic Chemistry, Japan, 1970) can be utilized. Specific examples include dyes such as azo dyes, metal complex salt azo dyes, pyrazolone azo dyes, naphthoquinone dyes, anthraquinone dyes, phthalocyanine dyes, naphthalocyanine dyes, carbonium dyes, quinoneimine dyes, methine dyes, cyanine dyes, squarylium dyes, (thio)pyrylium salts, metal thiolate complexes, indoaniline metal complex based dyes, oxonol dyes, diimonium dyes, aminium dyes, croconium dyes, and intermolecular CT dyes.

[0104]

Preferred examples of dyes include cyanine dyes described in JP-A Nos. 58-125246, 59-84356, 59-202829, and 60-78787; methine dyes described in JP-A Nos. 58-173696, 58-181690, and 58-194595; naphtoquinone dyes described in JP-A Nos. 58-112793, 58-224793, 59-48187, 59-73996, 60-52940, and 60-63744; squarylium dyes described in JP-A No. 58-112792; and cyanine dyes described in British Patent No. 434,875.

[0105]

Further, near infrared absorbing sensitizers described in USP No. 5,156,938 can also suitably be used. Moreover, substituted aryl benzo(thio)pyrylium salts described in USP No. 3,881,924, trimethine thiapyrylium salts described in JP-A No. 57-142645 (counterpart to USP No. 4,327,169), pyrylium

based compounds described in JP-A Nos. 58-181051, 58-220143, 59-41363, 59-84248, 59-84249, 59-146063, and 59-146061, cyanine dyes described in JP-A No. 59-216146, pentamethine thiopyrylium salts described in USP No. 4,283,475, and pyrylium compounds disclosed in JP-B Nos. 5-13514 and 5-19702 can also suitably be used.

[0106]

Near infrared absorbing dyes described as formulae (I) and (II) in USP No. 4,756,993 can also be enumerated as other preferred examples of the dye.

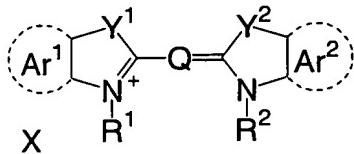
[0107]

Of these dyes are particularly preferable cyanine dyes, phthalocyanine dyes, oxonol dyes, squarylium dyes, pyrylium salts, thiopyrylium dyes, and nickel thiolate complexes.

[0108]

In addition, dyes represented by the following general formulae (a) to (f) are preferable because of their excellent light-heat conversion efficiency. Especially, cyanine dyes represented by the general formula (a) are the most preferable because when used in the invention, they give a high mutual action with the alkali-soluble resin and are excellent in stability and economy.

[0109]



General formula (a)

[0110]

In the general formula (a), R<sup>1</sup> and R<sup>2</sup> each independently represents an alkyl group having from 1 to 12 carbon atoms, which may be substituted with a substituent selected from an alkoxy group, an aryl group, an amide group, an alkoxycarbonyl group, a hydroxyl group, a sulfo group, and a carboxyl group. Y<sup>1</sup> and Y<sup>2</sup> each independently represents oxygen, sulfur, selenium, a dialkylmethylene group, or -CH=CH-. Ar<sup>1</sup> and Ar<sup>2</sup> each independently represents an aromatic hydrocarbon group, which may be substituted with a substituent selected from an alkyl group, an alkoxy group, a halogen atom, and an alkoxycarbonyl group, and the aromatic ring may be fused with Y<sup>1</sup> and Y<sup>2</sup> via adjacent continuous two carbon atoms.

[0111]

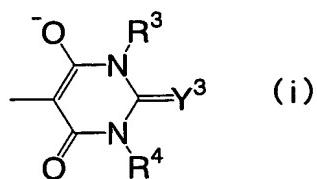
In the general formula (a), X represents a counter ion necessary for neutralizing charges, and in the case where the dye cation segment has an anionic substituent, X is not always necessary. Q represents a polymethine group selected from a trimethine group, a pentamethine group, a heptamethine group, a nonamethine group, and an undecamethine group; from the standpoints of wavelength adaptability against infrared rays to be

used for exposure and stability, Q is preferably a pentamethine group, a heptamethine group, or a nonmethine group; and it is preferred from the standpoint of stability to have a cyclohexene ring or cyclopentene ring containing continuous three methine chains on any one of carbon atoms.

[0112]

In the general formula (a), Q may be substituted with a group selected from an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, a dialkylamino group, a diarylamino group, a halogen atom, an alkyl group, an aralkyl group, a cycloalkyl group, an aryl group, an oxy group, an iminium salt group, and a substituent represented by the following general formula (I). Preferred examples of substituents include halogen atoms such as a chlorine atom, diarylamino groups such as a diphenylamino group, and arylthio groups such as a phenylthio group.

[0113]



[0114]

In the general formula (I), R<sup>3</sup> and R<sup>4</sup> each independently represents a hydrogen atom, an alkyl group having from 1 to 8

carbon atoms, or an aryl group having from 6 to 10 carbon atoms.

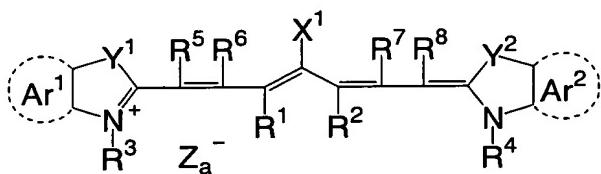
$Y^3$  represents an oxygen atom or a sulfur atom.

[0115]

Of the cyanine dyes represented by the general formula (a), in the case of exposure with infrared rays having a wavelength of 800 to 840 nm, heptamethinecyanine dyes represented by the following general formulae (a-1) to (a-4) are especially preferable.

[0116]

General formula (a-1)



[0117]

In the general formula (a-1),  $X^1$  represents a hydrogen atom or a halogen atom.  $R^1$  and  $R^2$  each independently represents a hydrocarbon group having from 1 to 12 carbon atoms. From the standpoint of storage stability of coating solutions for image forming layer, it is preferred that  $R^1$  and  $R^2$  are each a hydrocarbon group having two or more carbon atoms, and it is especially preferred that  $R^1$  and  $R^2$  are taken together to form a 5-membered or 6-membered ring.

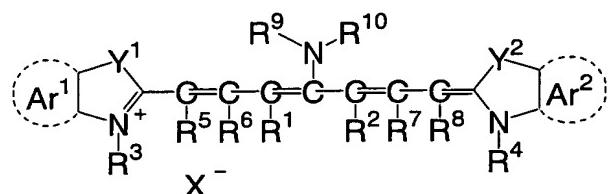
[0118]

In the general formula (a-1),  $Ar^1$  and  $Ar^2$  may be the same or

different and each represent an optionally substituted aromatic hydrocarbon group. Preferred examples of aromatic hydrocarbon groups include a benzene ring and a naphthalene ring. Preferred examples of substituents include hydrocarbon groups having not more than 12 carbon atoms, halogen atoms, and alkoxy groups having not more than 12 carbon atoms.  $Y^1$  and  $Y^2$  may be the same or different and each represent a sulfur atom or a dialkylmethylene group having not more than 12 carbon atoms.  $R^3$  and  $R^4$  may be the same or different and each represent an optionally substituted hydrocarbon groups having not more than 20 carbon atoms. Preferred examples of substituents include an alkoxy group having not more than 12 carbon atoms, a carboxyl group, and a sulfo group.  $R^5$ ,  $R^6$ ,  $R^7$  and  $R^8$  may be the same or different and each represent a hydrogen atom or a hydrocarbon group having not more than 12 carbon atoms, with a hydrogen atom being preferred from the standpoint of easiness of availability of raw materials.  $Za^-$  represents a counter anion necessary for neutralizing charges, and in the case where any one of  $R^1$  to  $R^8$  is substituted with an anionic substituent,  $Za^-$  is not necessary. From the standpoint of storage stability of coating solutions for image forming layer,  $Za^-$  is preferably a halogen ion, a perchloric acid ion, a tetrafluoroborate ion, a hexafluorophosphate ion, or a sulfonic acid ion, and particularly preferably a perchloric acid ion, a tetrafluoroborate ion, a hexafluorophosphate ion, or a sulfonic acid ion. The

heptamethine dyes represented by the general formula (a-1) can suitably be used in positive image forming materials, and especially, can preferably be used in so-called mutual action-releasing type positive photosensitive materials combined with a phenolic hydroxyl group-containing alkali-soluble resin.

[0119]



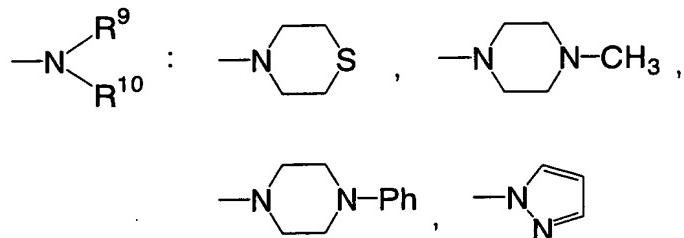
General formula (a-2)

[0120]

In the general formula (a-2), R<sup>1</sup> and R<sup>2</sup> each independently represents a hydrogen atom or a hydrocarbon group having from 1 to 12 carbon atoms, and R<sup>1</sup> and R<sup>2</sup> may bond with each other to form a ring structure. The ring to be formed is preferably a 5-membered ring or a 6-membered ring, and particularly preferably a 5-membered ring. Ar<sup>1</sup> and Ar<sup>2</sup> may be the same or different and each represent an optionally substituted aromatic hydrocarbon group. Preferred examples of aromatic hydrocarbon groups include a benzene ring and a naphthalene ring. Preferred examples of substituents on the aromatic hydrocarbon group include hydrocarbon groups having not more than 12 carbon atoms, halogen atoms, and alkoxy groups, alkoxy carbonyl groups, alkylsulfonyl groups and halogenated alkyl groups each having not

more than 12 carbon atoms, with electron-withdrawing substituents being particularly preferred. Y<sup>1</sup> and Y<sup>2</sup> may be the same or different and each represent a sulfur atom or a dialkylmethylene group having not more than 12 carbon atoms. R<sup>3</sup> and R<sup>4</sup> may be the same or different and each represent an optionally substituted hydrocarbon group having not more than 20 carbon atoms. Preferred examples of substituents include an alkoxy group having not more than 12 carbon atoms, a carboxyl group, and a sulfo group. R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> may be the same or different and each represent a hydrogen atom or a hydrocarbon group having not more than 12 carbon atoms, with a hydrogen atom being preferred from the standpoint of easiness of availability of raw materials. R<sup>9</sup> and R<sup>10</sup> may be the same or different and each represent an optionally substituted aromatic hydrocarbon group having from 6 to 10 carbon atoms, an optionally substituted alkyl group having from 1 to 8 carbon atoms, or a hydrogen atom, or may bond with each other to form a ring having any one of the following structures.

[0121]

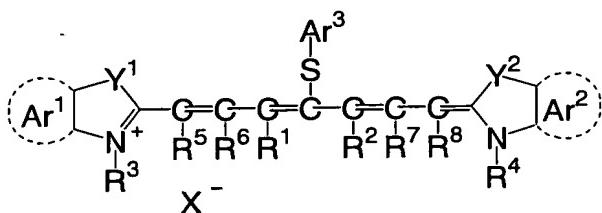


[0122]

In the general formula (a-2), R<sup>9</sup> and R<sup>10</sup> are most preferably an aromatic hydrocarbon group such as a phenyl group.

X<sup>-</sup> represents a counter anion necessary for neutralizing charges and is synonymous with ZA<sup>-</sup> in the foregoing general formula (a-1).

[0123]

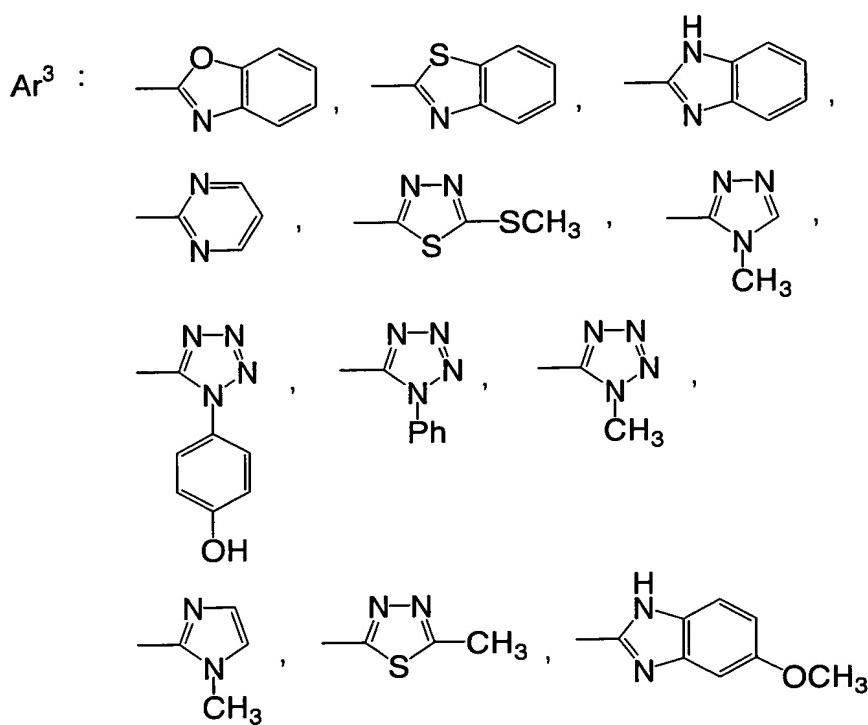


[0124]

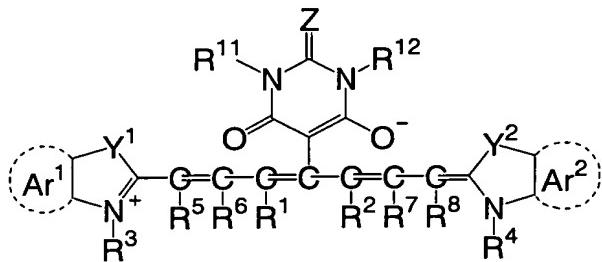
In the general formula (a-3), R<sup>1</sup> to R<sup>8</sup>, Ar<sup>1</sup>, Ar<sup>2</sup>, Y<sup>1</sup>, Y<sup>2</sup> and X<sup>-</sup> are respectively synonymous with those in the foregoing general formula (a-2). Ar<sup>3</sup> represents an aromatic hydrocarbon group such as a phenyl group and a naphthyl group or a monocyclic or polycyclic heterocyclic group containing at least one of nitrogen, oxygen and sulfur atoms, and preferably a heterocyclic group selected from the group consisting of thiazole based, benzothiazole based, naphthothiazole based, thianaphtheno-7,6,4,5-thiazole based, oxazole based, benzoxazole based, naphthoxazole based, selenazole based, benzoselenazole based, naphthoselenazole based, thiazoline based, 2-quinoline based, 4-quinolin based, 1-isoquinoline based, 3-isoquinoline based, benzimidazole based,

3,3-dialkylbenzoindolenine based, 2-pyridine based, 4-pyridine based, 3,3-dialkylbenzo[e]indole based, tetrazole based, triazole based, pyrimidine based, and thiadiazole based groups. As the heterocyclic group, the following structures are the most preferable.

[0125]



[0126]



General formula (a-4)

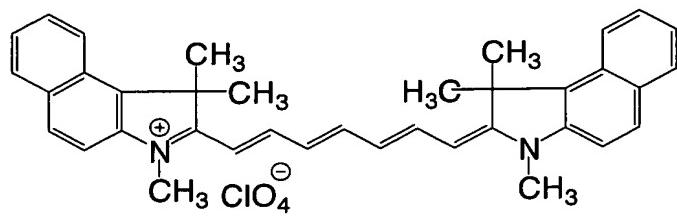
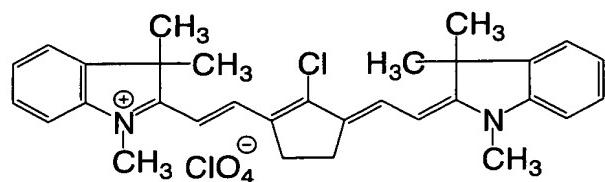
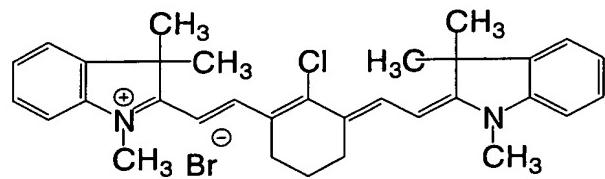
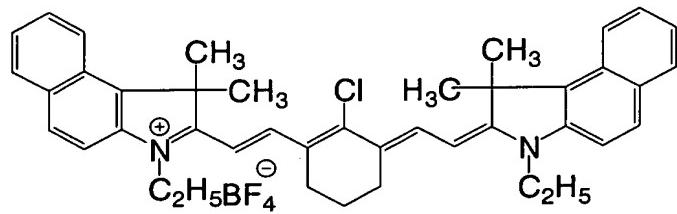
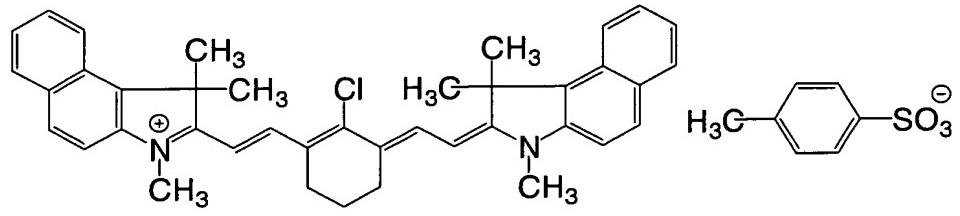
[0127]

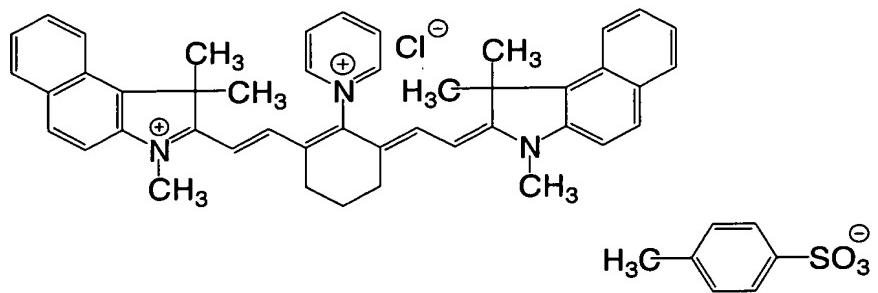
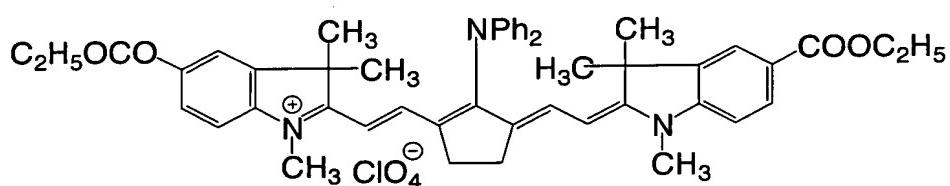
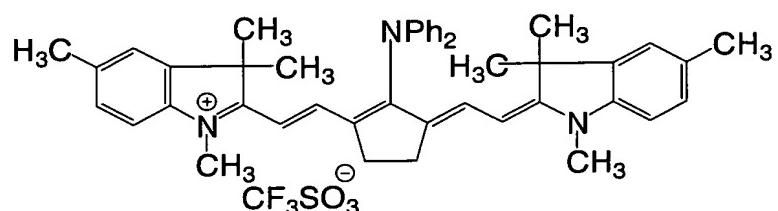
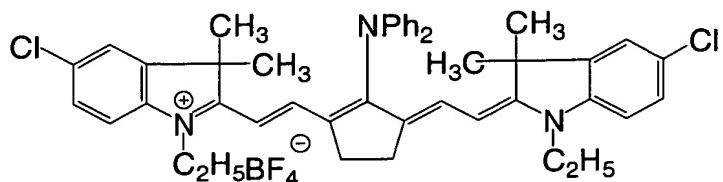
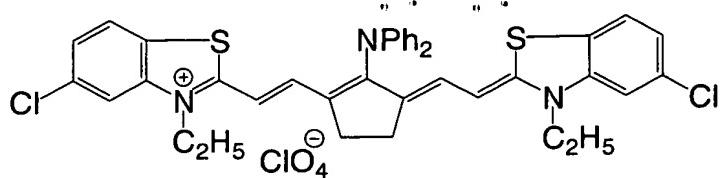
In the general formula (a-4), R<sup>1</sup> to R<sup>8</sup>, Ar<sup>1</sup>, Ar<sup>2</sup>, Y<sup>1</sup> and Y<sup>2</sup> are respectively synonymous with those in the foregoing general formula (a-2). R<sup>11</sup> and R<sup>12</sup> may be the same or different and each represent a hydrogen atom, an allyl group, a cyclohexyl group, or an alkyl group having from 1 to 8 carbon atoms. Z represents an oxygen atom or a sulfur atom.

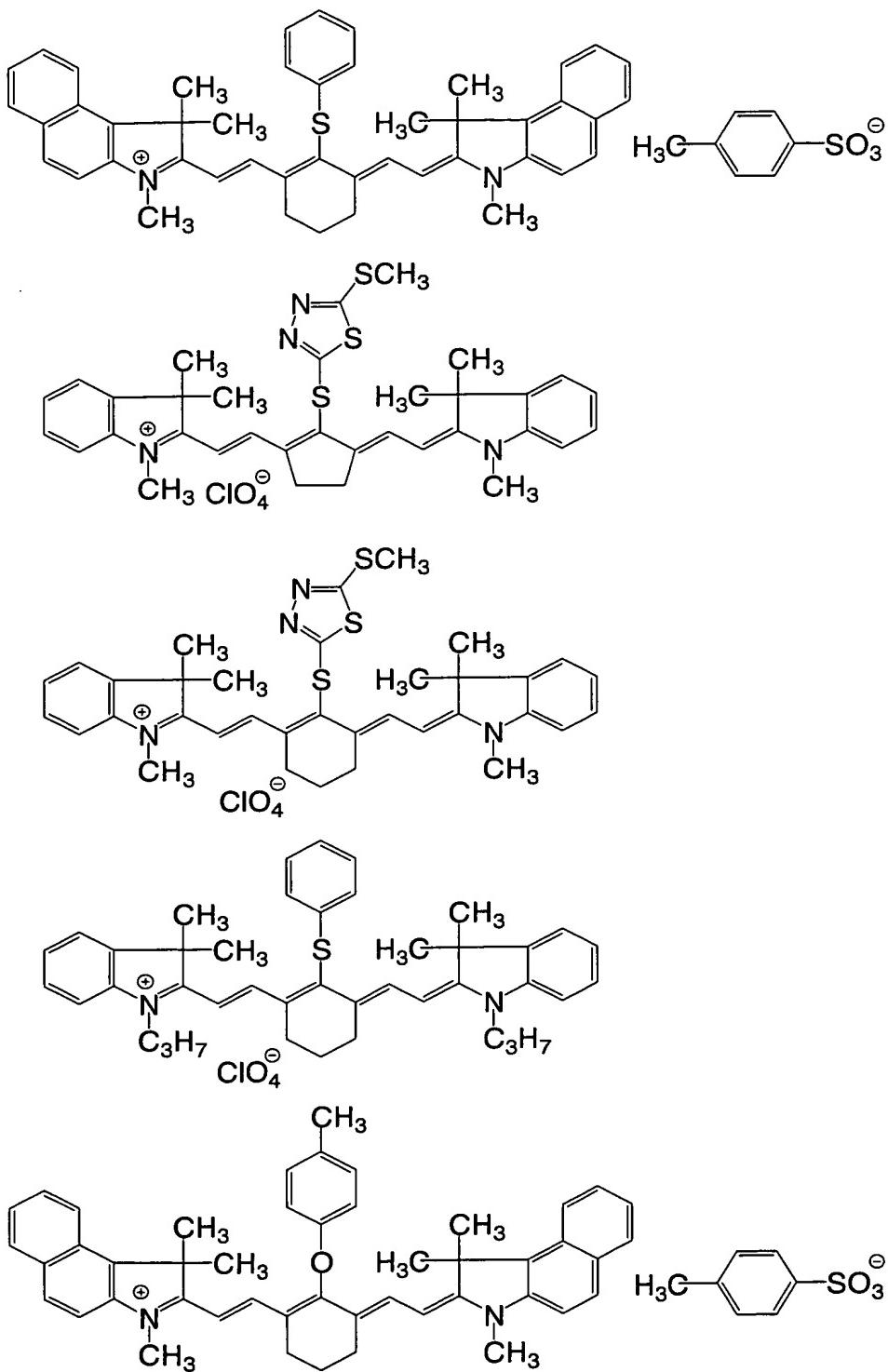
[0128]

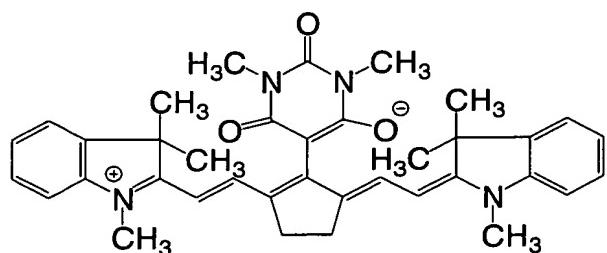
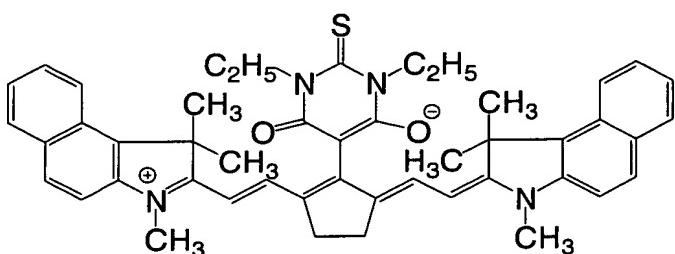
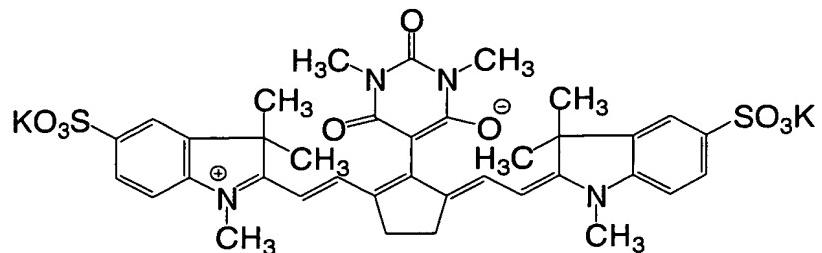
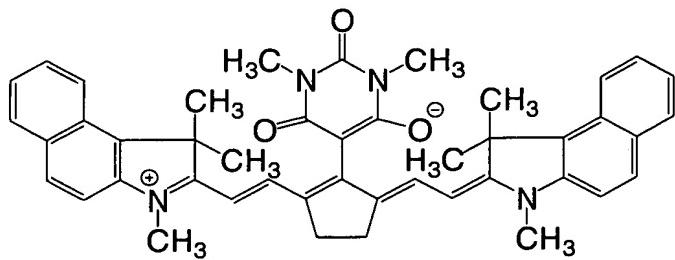
In the invention, specific examples of cyanine dyes represented by the general formula (a) that can suitably be used include those described in paragraphs [0017] to [0019] of JP-A No. 2001-133969, paragraphs [0012] to [0038] of JP-A No. 2002-40638, and paragraphs [0012] to [0023] of JP-A No. 2002-23360, in addition to those enumerated below.

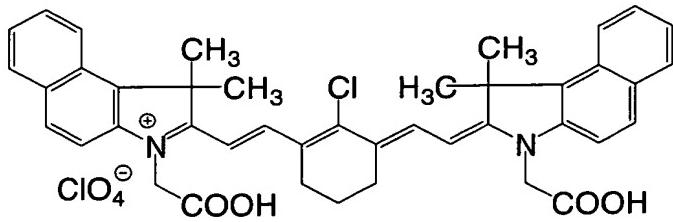
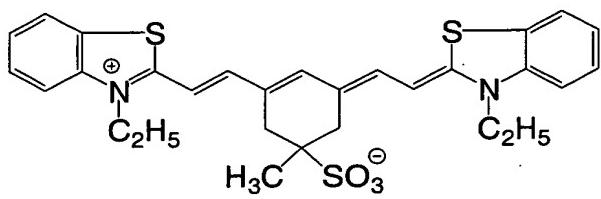
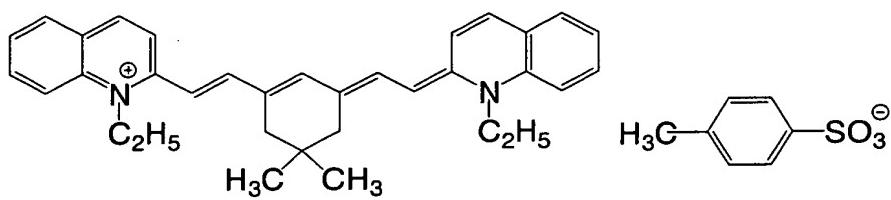
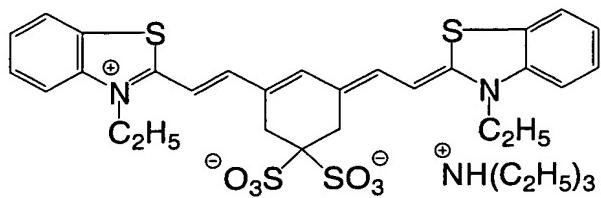
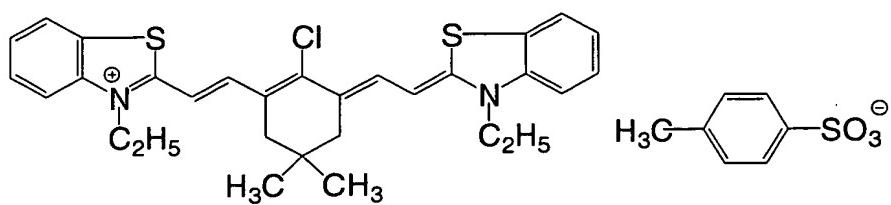
[0129]

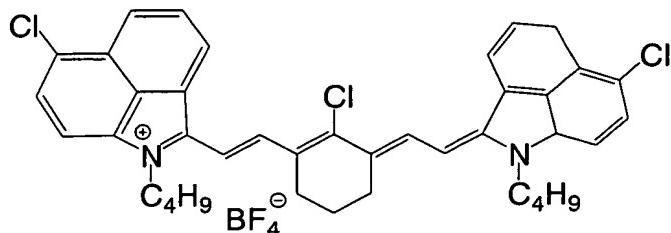
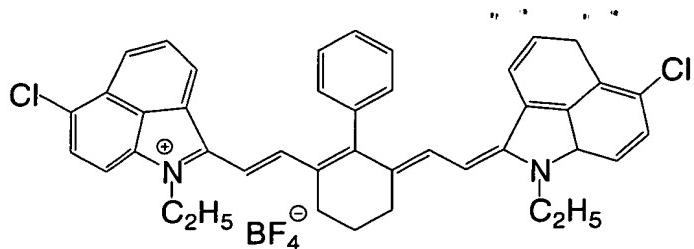






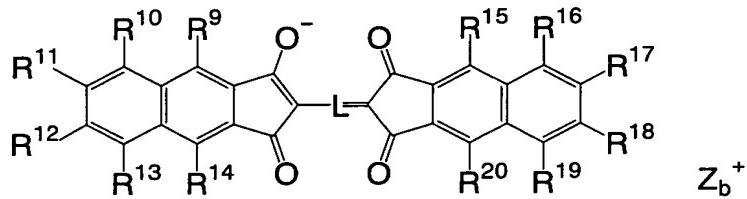






[0135]

General formula (b)



[0136]

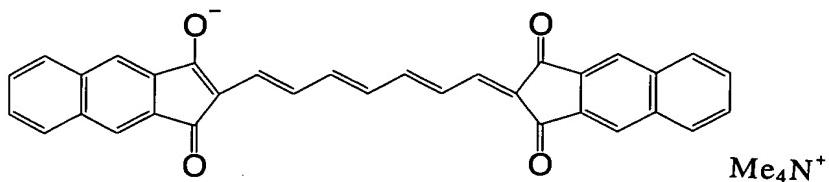
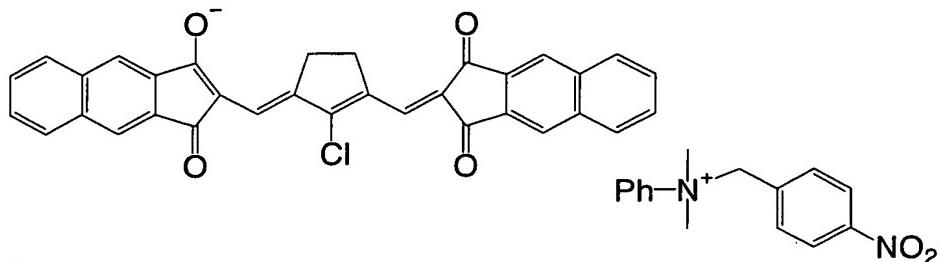
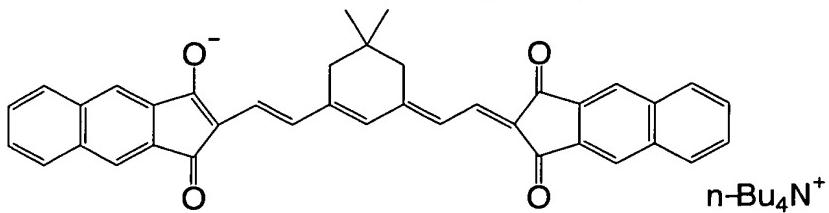
In the general formula (b), L represents a methine chain having 7 or more conjugated carbons. The methine chain may have a substituent, and substituents may bond with each other to form a ring structure.  $Zb^+$  represents a counter cation. Preferred examples of counter cations include ammonium, iodonium, sulfonium, phosphonium, pyridinium, and alkali metal cations (such as  $Na^+$ ,  $K^+$ , and  $Li^+$ ).  $R^9$  to  $R^{14}$  and  $R^{15}$  to  $R^{20}$  each independently represents a hydrogen atom or a substituent selected from a halogen atom, a cyano group, an alkyl group, an

aryl group, an alkenyl group, an alkynyl group, a carbonyl group, a thio group, a sulfonyl group, a sulfinyl group, an oxy group, and an amino group, or a substituent comprising a combination of two or three of these groups, and may bond with each other to form a ring structure. Here, in the general formula (b), ones in which L represents a methine chain having 7 conjugated carbons, and R<sup>9</sup> to R<sup>14</sup> and R<sup>15</sup> to R<sup>20</sup> are all a hydrogen atom are preferable from the standpoints of easiness of availability of raw materials and effect.

[0137]

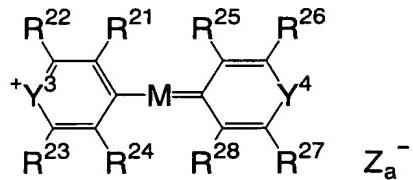
In the present invention, specific examples of dyes represented by the general formula (b), which can suitably be used, will be given below.

[0138]



[0139]

General formula (c)



[0140]

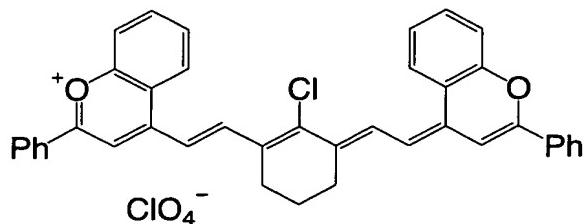
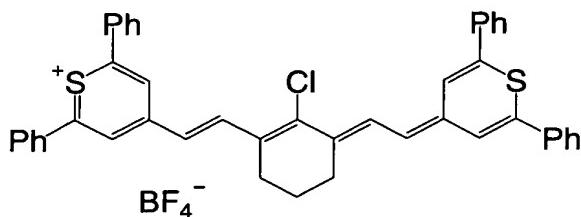
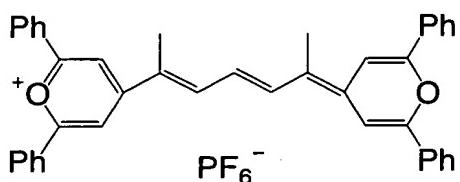
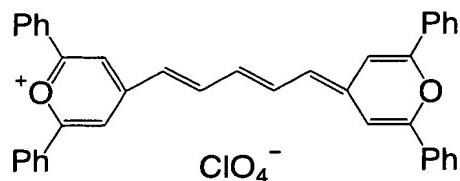
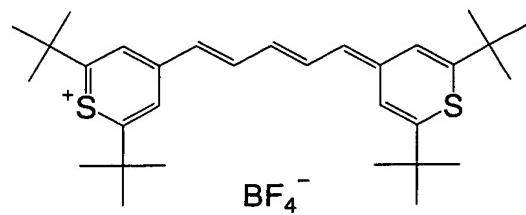
In the general formula (c),  $\text{Y}^3$  and  $\text{Y}^4$  each independently represents an oxygen atom, a sulfur atom, a selenium atom, or a tellurium atom.  $\text{M}$  represents a methine chain having at least five or more conjugated carbon atoms.  $\text{R}^{21}$  to  $\text{R}^{24}$  and  $\text{R}^{25}$  to  $\text{R}^{28}$  may be the same or different and each represent a hydrogen atom, a halogen atom, a cyano group, an alkyl group, an aryl group, an

alkenyl group, an alkynyl group, a carbonyl group, a thio group, a sulfonyl group, a sulfinyl group, an oxy group, or an amino group.  $Za^-$  represents a counter anion and is synonymous with  $Za^-$  in the foregoing general formula (a).

[0141]

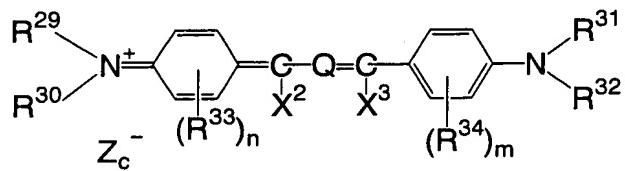
In the present invention, specific examples of dyes represented by the general formula (c), which can suitably be used, will be given below.

[0142]



[0143]

General formula (d)



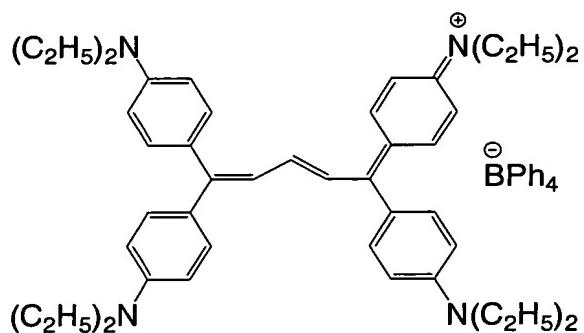
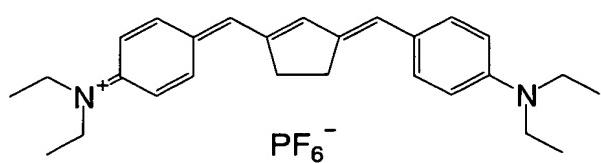
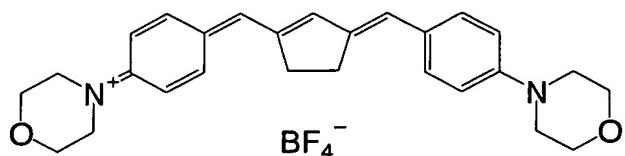
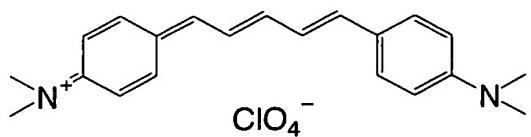
[0144]

In the general formula (d), R<sup>29</sup> to R<sup>32</sup> each independently represents a hydrogen atom, an alkyl group, or an aryl group. R<sup>33</sup> and R<sup>34</sup> each independently represent an alkyl group, a substituted oxy group, or a halogen atom. n and m each independently represents an integer from 0 to 4. R<sup>29</sup> and R<sup>30</sup>, or R<sup>31</sup> and R<sup>32</sup> may bond with each other to form a ring, at least one of R<sup>29</sup> and R<sup>30</sup> may bond with R<sup>33</sup> to form a ring, and at least one of R<sup>31</sup> and R<sup>32</sup> may bond with R<sup>34</sup> to form a ring. Further, in the case when a plural number of R<sup>33</sup> or R<sup>34</sup> are present, the plurality of R<sup>33</sup> or the plurality of R<sup>34</sup> may bond with each other to form a ring. X<sup>2</sup> and X<sup>3</sup> each independently represents a hydrogen atom, an alkyl group, or an aryl group. Q represents an optionally substituted trimethine group or pentamethine group and may form a ring structure together with a divalent organic group. Zc represents a counter anion and is synonymous with Za<sup>-</sup> in the foregoing general formula (a).

[0145]

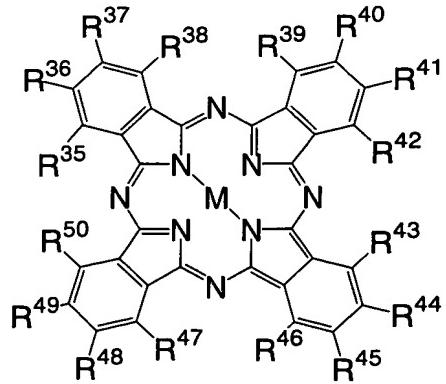
In the present invention, specific examples of dyes represented by the general formula (d), which can suitably be used, will be given below.

[0146]



[0147]

### General formula (e)



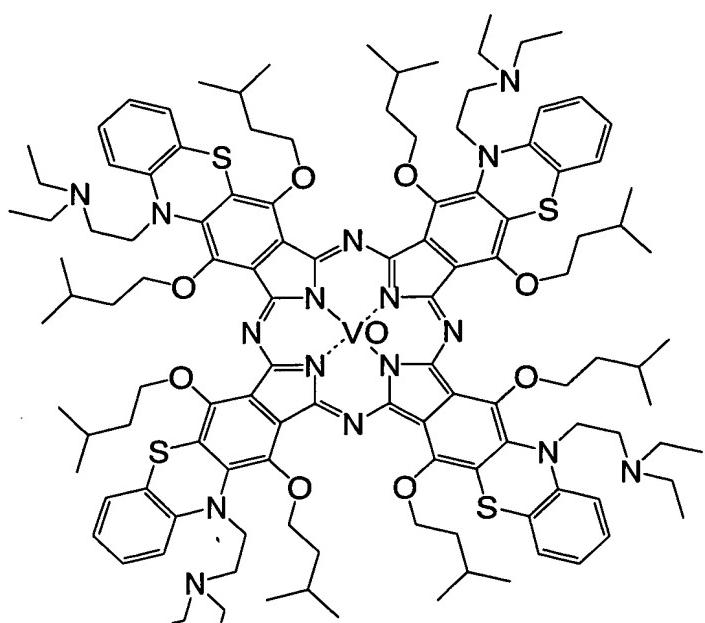
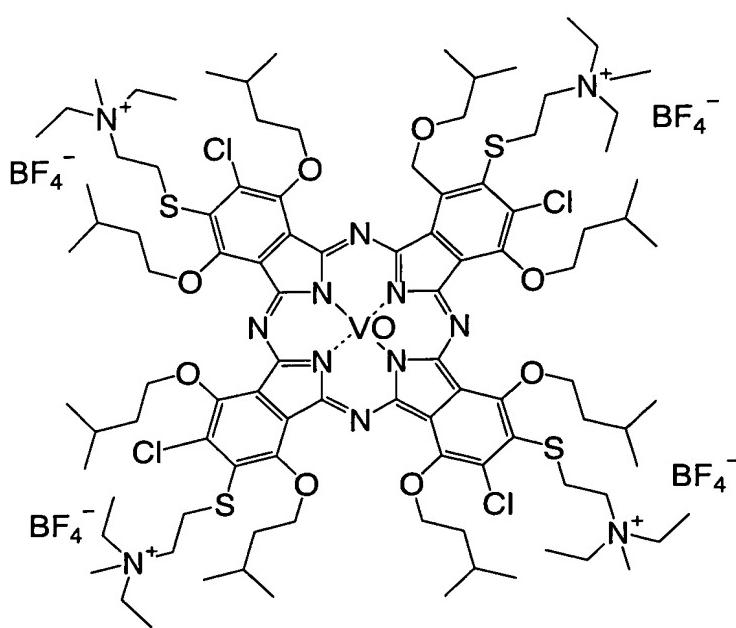
[0148]

In the general formula (e), R<sup>35</sup> to R<sup>50</sup> each independently represents a hydrogen atom, a halogen atom, a cyano group, an alkyl group, an aryl group, an alkenyl group, an alkynyl group, a hydroxyl group, a carbonyl group, a thio group, a sulfonyl group, a sulfinyl group, an oxy group, an amino group, or an onium salt structure, and in the case where a substituent can be introduced, these groups may have a substituent. M represents two hydrogen atoms, a metal atom, a halometal group, or an oxy metal group. Examples of metal atoms to be contained therein include atoms belonging to the Groups IA, IIA, IIIB and IVB of the Periodic Table, transition metals of the first, second and third periods, and lanthanoid elements. Of these, copper, nickel, magnesium, iron, zinc, tin, cobalt, aluminum, titanium, and vanadium are preferable, and vanadium, nickel, zinc, and tin are particularly preferable. For making the valence proper, these metal atoms may be bonded to an oxygen atom, a halogen atom, and the like.

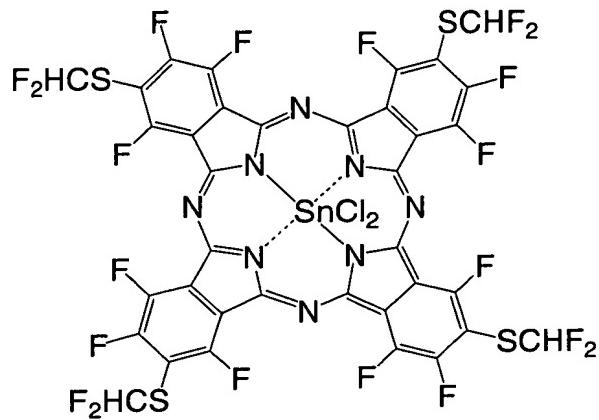
[0149]

In the present invention, specific examples of dyes represented by the general formula (e), which can suitably be used, will be given below.

[0150]

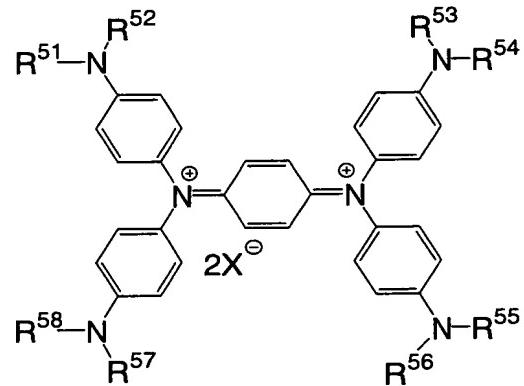


[0151]

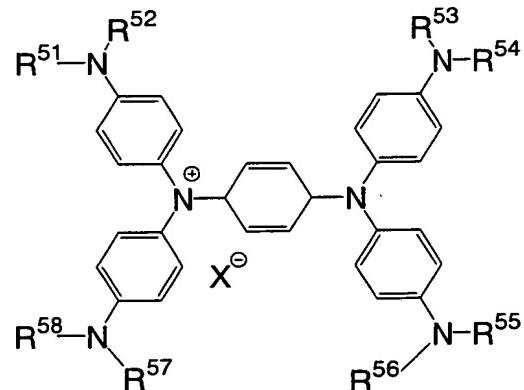


[0152]

General formula (f-1)



General formula (f-2)



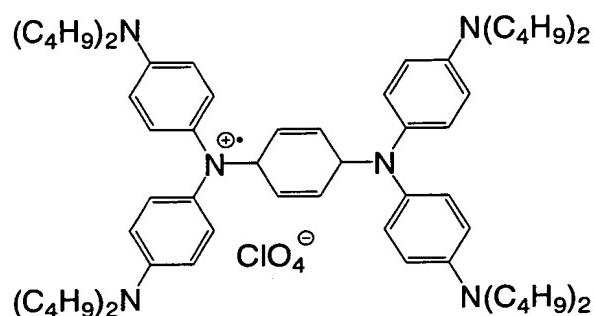
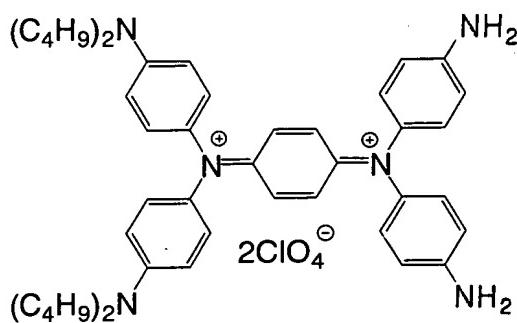
[0153]

In the general formulae (f-1) and (f-2), R<sup>51</sup> to R<sup>58</sup> each independently represents a hydrogen atom or an optionally substituted alkyl group or aryl group. X<sup>-</sup> is synonymous with X in the foregoing general formula (a-2).

[0154]

In the present invention, specific examples of dyes represented by the general formulae (f-1) and (f-2), which can suitably be used, will be given below.

[0155]



[0156]

As Light-heat Converting agents other than those described above, dyes having a plurality of chromophores described in JP-A No. 2001-242613, coloring materials comprising a high-molecular compound having a chromophore covalently connected thereto described in JP-A No. 2002-97384 and USP No. 6,124,425, anionic dyes described in USP No. 6,248,893, and dyes having a surface orientating group described in JP-A No. 2001-347765 can suitably be used.

[0157]

As pigments that are used as the Light-heat Converting agent in the invention can be utilized commercially available pigments and pigments described in Color Index (C.I.) Handbook,

Saishin Ganryo Binran (The Newest Pigment Handbook) (edited by The Japan Pigment Technology Association, 1977), Saishin Ganryo Oyo Gijutsu (The Newest Pigment Application Technology) (published by CMC Publishing Co., Ltd., 1986), and Insatsu Inki Gijutsu (Printing Ink Technology) (published by CMC Publishing Co., Ltd., 1984).

[0158]

As kinds of pigments are enumerated black pigment, yellow pigments, orange pigments, brown pigments, red pigments, violet pigments, blue pigments, green pigments, fluorescent pigments, metallic flake pigments, and polymer-binding pigments. Specifically, insoluble azo pigments, azo lake pigments, condensed azo pigments, chelate azo pigments, phthalocyanine based pigments, anthraquinone based pigments, perylene or perynone based pigments, thioindigo based pigments, quinacridone based pigments, dioxazine based pigments, isoindolinone based pigments, quinophthalone based pigments, dyeing lake pigments, azine pigments, nitroso pigments, nitro pigments, natural pigments, fluorescent pigments, inorganic pigments, and carbon black. Of these is preferable carbon black.

[0159]

These pigments may be used without being subjected to surface processing, or may be used after being subjected to surface processing. As the method of the surface processing, there may be considered a method of coating the surface of the

pigment with a resin or a wax, a method of adhering a surfactant to the surface of the pigment, and a method of a reactive substance (such as silane coupling agents, epoxy compounds, and polyisocyanates) to the surface of the pigment. These surface processing methods are described in *Kinzoku Sekken No Seishitsu To Oyo* (Nature and Application of Metallic Soap) (published by Saiwai Shobo Co., Ltd.), *Insatsu Ink Gijutsu* (Printing Ink Technology) (published by CMC Publishing Co., Ltd., 1984), and *Saishin Ganryo Oyo Gijutsu* (The Newest Pigment Application Technology) (published by CMC Publishing Co., Ltd., 1986).

[0160]

The pigment preferably has a particle size in the range of 0.01  $\mu\text{m}$  to 10  $\mu\text{m}$ , more preferably from 0.05  $\mu\text{m}$  to 1  $\mu\text{m}$ , and particularly preferably from 0.1  $\mu\text{m}$  to 1  $\mu\text{m}$ . The particle size that is less than 0.01  $\mu\text{m}$  is not preferable from the viewpoint of stability of pigment dispersion in coating solutions for image forming layer, and the particle size greater than 10  $\mu\text{m}$  is not preferable from the viewpoint of uniformity of image forming layer.

[0161]

As a method of dispersing the pigment, known dispersing technologies used in ink production or toner production can be used. Examples of dispersing machines include ultrasonic dispersing units, sand mills, attritors, pearl mills, super mills, ball mills, impellers, dispersers, KD mills, colloid mills, dynatrons, three-roll mills, and pressure kneaders. The details

are described in Saishin Ganryo Oyo Gijutsu (The Newest Pigment Application Technology) (published by CMC Publishing Co., Ltd., 1986).

[0162]

The pigment or dye in the light-heat converting agent (C) can be added in an amount of 0.01 to 50 % by mass, preferably from 0.1 to 10 % by mass, and particularly preferably 0.5 to 10 % by mass in the case of the dye and 0.1 to 10 % by mass in the case of the pigment, respectively on a basis of the whole of solid contents constituting the image forming layer. When the amount of the pigment or dye added is less than 0.01 % by mass, the sensitivity tends to decrease. When the amount of the pigment or dye added is greater than 50 % by mass, there is a possibility that the uniformity or durability of an image forming layer may be adversely affected. Further, the dye or pigment to be used may be used singly or in admixture of two or more thereof. For corresponding to exposing machines with a plurality of wavelengths, it is preferably employed to jointly use dyes or pigments having a different absorption wavelength.

[0163]

[Other components]

In the invention, in forming the positive image forming layer, various additives can be added as the need arises. From the viewpoint of enhancing dissolution inhibition of image areas into the developing solution, it is preferred to jointly use substances

that are heat decomposable and in a non-decomposed state, substantially reduce dissolution of the alkali-soluble high-molecular compound, such as other onium salts, o-quinonediazide compounds, aromatic sulfone compounds, and aromatic sulfonic acid ester compounds. Examples of other onium salts include oniums other than the onium salts falling within the scope of the compound represented by the foregoing general formula (1), such as diazonium salts, ammonium salts, phosphonium salts, iodonium salts, sulfonium salts, selenonium salts, arsonium salts, and azinium salts.

[0164]

Suitable examples of other onium salts that are used in the invention include diazonium salts described in S.I. Schlesinger, Photogr. Sci. Eng., 18, 387 (1974), T.S. Bal, et al., Polymer, 21, 423 (1980), and JP-A No. 5-158230; ammonium salts described in USP Nos. 4,069,055 and 4,069,056 and JP-A No. 3-140140; phosphonium salts described in D.C. Necker, et al., Macromolecules, 17, 2468 (1984), C.S. Wen, et al., Teh, Proc. Conf. Rad. Curing, ASIA, p.478, Tokyo, Oct (1988), and USP Nos. 4,069,055 and 4,069,056; iodonium salts described in J.V. Crivello, et al., Macromolecules, 10(6), 1307 (1977), Chem. & Eng. News, Nov., 28, p.31 (1988), European Patent No. 104,143, USP Patent Nos. 5,041,358 and 4,491,628, and JP-A Nos. 2-150848 and 2-296514; sulfonium salts described in J.V. Crivello, et al., Polymer J., 17, 73 (1985), J.V. Crivello, et al., J. Org. Chem., 43,

3055 (1978), W.R. Watt, et al., J. Polymer Sci., Polymer Chem. Ed., 22, 1789 (1984), J.V. Crivello, et al., Polymer Bull., 14, 279 (1985), J.V. Crivello, et al., Macromolecules, 14(5), 1141 (1981), J.V. Crivello, et al., Polymer Sci., Polymer Chem. Ed., 17, 2877 (1979), European Patent Nos. 370,693, 233,567, 297,443 and 297,442, USP Nos. 4,933,377, 3,902,114, 5,041,358, 4,491,628, 4,760,013, 4,734,444 and 2,833,827, and German Patent Nos. 2,904,626, 3,604,580 and 3,604,581; selenonium salts described in J.V. Crivello, et al., Macromolecules, 10(6), 1307 (1977) and J.V. Crivello, et al., J. Polymer Sci., Polymer Chem. Ed., 17, 1047 (1979); and arsonium salts described in C.S. Wen, et al., Teh, Proc. Conf. Rad. Curing, ASIA, p.478, Tokyo, Oct (1988).

[0165]

Of these other onium salts are particularly preferable diazonium salts. Further, particularly suitable examples of diazonium salts are those described in JP-A No. 5-158230.

[0166]

Examples of counter ions of the foregoing other onium salts include tetrafluoroboric acid, hexafluorophosphoric acid, triisopropylnaphthalenesulfonic acid, 5-nitro-o-toluenesulfonic acid, 5-sulfosalicylic acid, 2,5-dimethylbenzenesulfonic acid, 2,4,6-trimethylbenzenesulfonic acid, 2-nitrobenzenesulfonic acid, 3-chlorobenzenesulfonic acid, 3-bromobenzenesulfonic acid, 2-fluorocaprylnaphthalenesulfonic acid, dodecylbenzenesulfonic acid, 1-naphthol-5-sulfonic acid,

2-methoxy-4-hydroxy-5-benzoylbenzenesulfonic acid, and p-toluenesulfonic acid. Of these are particularly suitable hexafluorophosphoric acid, triisopropylnaphthalenesulfonic acid, and alkyl aromatic sulfonic acids such as 2,5-dimethylbenzenesulfonic acid.

[0167]

Suitable examples of quinonediazides include o-quinonediazide compounds. The o-quinonediazide compound to be used in the invention is a compound containing at least one o-quinonediazide group, whose alkali solubility increases by heat decomposition, and compounds having various structures can be used. Namely, the o-quinonediazide assists dissolution of photosensitive materials due to both of an effect in which it loses dissolution inhibition of a binder by heat decomposition and an effect in which the o-quinonediazide itself converts into an alkali-soluble substance. Examples of o-quinonediazide compounds that are used in the invention include compounds described in J. Kosar, Light-Sensitive Systems, pp.339-352, John Wiley & Sons. Inc. Especially, sulfonic acid esters or sulfonic acid acids of o-quinonediazide reacted with various aromatic polyhydroxy compounds or aromatic amino compounds are suitable. Further, esters of benzoquinone-(1,2)-diazidosulfonic acid chloride or naphthoquinone-(1,2)-diazido-5-sulfonic acid chloride and a pyrrogallol-acetone resin described in JP-B No. 43-28403 and esters of benzoquinone-(1,2)-diazidosulfonic acid

chloride or naphthoquinone-(1,2)-diazido-5-sulfonic acid chloride and a phenol-formaldehyde resin described in USP Nos. 3,046,120 and 3,188,210 are also suitably used.

[0168]

In addition, esters of naphthoquinone-(1,2)-diazido-4-sulfonic acid chloride and a phenol-formaldehyde resin or a cresol-formaldehyde resin and esters of naphthoquinone-(1,2)-diazido-4-sulfonic acid chloride and a pyrrogallol-acetone resin are suitably used, too. Besides, useful o-quinonediazide compounds are reported in and known by various patents such as JP-A Nos. 47-5303, 48-63802, 48-63803, 48-96575, 49-38701 and 48-13354, JP-B Nos. 41-11222, 45-9610 and 49-17481, USP Nos. 2,797,213, 3,454,400, 3,544,323, 3,573,917, 3,674,495 and 3,785,825, British Patent Nos. 1,227,602, 1,251,345, 1,267,005, 1,329,888 and 1,330,932, and German Patent No. 854,890.

[0169]

The addition amount of the o-quinonediazide compound is preferably in the range of 1 to 50 % by mass, more preferably 5 to 30 % by mass, and particularly preferably 10 to 30 % by mass based on the whole of solid contents of the image forming material. Such o-quinonediazide compounds may be used alone or in admixture.

[0170]

The addition amount of other additives than the

*o*-quinonediazide compound is preferably in the range of 1 to 50 % by mass, more preferably 5 to 30 % by mass, and particularly preferably 10 to 30 % by mass based on the whole of solid contents of the image forming material. Incidentally, in the present invention, it is preferred to contain the additives and the binder in the same layer.

[0171]

For the purpose of further enhancing the sensitivity, cyclic acid anhydrides, phenols, and organic acids can be used jointly. Specific examples of cyclic acid anhydrides include phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, 3,6-endooxy- $\Delta^4$ -tetrahydrophthalic anhydride, tetrachlorophthalic anhydride, maleic anhydride, chloromaleic anhydride,  $\alpha$ -phenylmaleic anhydride, succinic anhydride, and pyromellitic anhydride, as described in USP No. 4,115,128.

Examples of phenols include bisphenol A, p-nitrophenol, p-ethoxyphenol, 2,4,4'-trihydroxybenzophenone, 2,3,4-trihydroxybenzophenone, 4-hydroxybenzophenone, 4,4',4"-trihydroxytriphenylmethane, and 4,4',3",4"-tetrahydroxy-3,5,3',5'-tetramethyltriphenylmethane. In addition, examples of organic acids include sulfonic acids, sulfinic acids, alkylsulfuric acids, phosphonic acids, phosphoric acid esters, and carboxylic acids, as described in JP-A Nos. 60-88942 and 2-96755. Specific examples include p-toluenesulfonic acid, dodecylbenzenesulfonic acid, p-toluenesulfinic acid, ethylsulfuric

acid, phenylphosphonic acid, phenylphosphinic acid, phenyl phosphonate, phenyl phosphinate, phenyl phosphate, diphenyl phosphate, benzoic acid, isophthalic acid, adipic acid, p-toluylic acid, 3,4-dimethoxybenzoic acid, phthalic acid, terephthalic acid, 4-cyclohexene-1,2-dicarboxylic acid, erucic acid, laurylic acid, n-undecanoic acid, and ascorbic acid. A proportion of the cyclic acid anhydrides, phenols or organic acids occupying in the image forming material is preferably from 0.05 to 20 % by mass, more preferably from 0.1 to 15 % by mass, and particularly preferably from 0.1 to 10 % by mass.

[0172]

In the present invention, for widening stability of processings against the development condition, nonionic surfactants described in JP-A Nos. 62-251740 and 3-208514, ampholytic surfactants described in JP-A Nos. 59-121044 and 4-13149, cyclohexane based compounds described in European Patent No. 950,517, and fluorine-containing monomer copolymers described in JP-A No. 11-288093 can be added in the coating solution for image forming layer.

Specific examples of nonionic surfactants include sorbitan tristearate, sorbitan monopalmitate, sorbitan trioleate, stearic acid monoglyceride, and polyoxyethylene nonylphenyl ether.

Specific examples of ampholytic surfactants include alkyl di(aminoethyl) glycines, alkyl polyaminoethyl glycine hydrochlorides, 2-alkyl-N-carboxyethyl-N-hydroxyethyl

imidazolinium betaines, and N-tetradecyl-N,N-betaines (such as a trade name: AMOGEN K, manufactured by Daiichi Kogyo K.K.).

As siloxane based compounds, block copolymers of dimethylsiloxane and a polyalkylene oxide are preferable. Specific examples include polyalkylene oxide-modified silicones such as DBE-224, DBE-621, DBE-712, DBP-732 and DBP-534 (trade names, manufactured by Chisso Corporation) and TEGO GLIDE 100 (a trade name, manufactured by Tego Chemie Service GmbH, Germany).

A proportion of the nonionic surfactants or ampholytic surfactants occupying in the image forming material is preferably from 0.05 to 15 % by mass, and more preferably from 0.1 to 5 % by mass.

[0173]

In the image forming layer of the present invention, printing-out agents for obtaining visible images immediately after heating by exposure and dyes or pigments as image coloring agents can be added.

Representative examples of printing-out agents include combinations of a compound capable of releasing an acid upon heating by exposure (photo acid-releasing agent) and an organic dye capable of forming a salt. Specific examples include combinations of an o-naphthoquinonediazido-4-sulfonic acid halogenide and a salt-forming organic dye described in JP-A Nos. 50-36209 and 53-8128 and combinations of a trihalomethyl

compound and a salt-forming organic dye described in JP-A Nos. 53-36223, 54-74728, 60-3626, 61-143748, 61-151644, and 63-58440. Examples of such trihalomethyl compounds include oxazole based compounds and triazine based compounds, and both of these compounds are excellent in stability with time and give distinct print-out images.

[0174]

As image coloring agents, other dyes than the foregoing salt-forming organic dyes can be used. Examples of suitable dyes inclusive of salt-forming organic dyes include oil-soluble dyes and basic dyes. Specific examples include Oil Yellow #101, Oil Yellow #103, Oil Pink #312, Oil Green BG, Oil Blue BOS, Oil Blue #603, Oil Black BY, Oil Black BS and Oil Black T-505 (all being manufactured by Orient Chemical Industries, Ltd.), Victoria Pure Blue, Crystal Violet (CI42555), Methyl Violet (CI42535), Ethyl Violet, Rhodamine B (CI145170B), Malachite Green (CI42000), and Methylene Blue (CI52015). Further, dyes described in JP-A No. 62-293247 are particularly preferable. These dyes are used in a proportion of 0.01 to 10 % by mass, and preferably 0.1 to 3 % by mass based on the whole of solid contents of the image forming material. Further, for imparting flexibility of coating film, and the like, if desired, plasticizers are added in the image forming material of the invention. Examples include butyl phthalyl, polyethylene glycol, tributyl citrate, diethyl phthalate, dibutyl phthalate, dihexyl phthalate, dioctyl phthalate, tricresyl

phosphate, tributyl phosphate, trioctyl phosphate, tetrahydrofurfuryl oleate, and oligomers and polymers of acrylic acid or methacrylic acid.

[0175]

Besides, epoxy compounds, vinyl ethers, and additionally, hydroxymethyl group-containing phenol compounds and alkoxyethyl group-containing phenol compounds described in JP-A No. 8-276558, and crosslinking compounds having an alkaline dissolution inhibiting action described in JP-A No. 11-160860 as previously proposed by the present inventors can properly be added according to the purpose.

[0176]

The image forming material of the invention is one comprising this image forming layer formed on a proper support and can be applied to various utilizations such as planographic printing plate precursors, colorproof materials, and display materials, and is especially useful as a heat mode type planographic printing plate precursor that can be subjected to direct plate making upon exposure with infrared laser.

[0177]

<Planographic printing plate precursor>

An embodiment in which the image forming material of the invention is applied as a planographic printing plate precursor will be specifically described below while referring to examples.

[0178]

[Image forming layer]

A planographic printing plate precursor to which the image forming material of the invention is applied can be produced by dissolving components of coating solutions of image forming layer in a solvent and coating the solution on a proper support.

Further, a protective layer, a resin interlayer, a backcoat layer, and the like can be formed similarly according to the purpose.

Examples of solvents to be used herein include ethylene dichloride, cyclohexanone, methyl ethyl ketone, methanol, ethanol, propanol, ethylene glycol monomethyl ether, 1-methoxy-2-propanol, 2-methoxyethyl acetate, 1-methoxy-2-propyl acetate, dimethoxyethane, methyl lactate, ethyl lactate, N,N-dimethylacetamide, N,N-dimethylformamide, tetramethylurea, N-methylpyrrolidone, dimethyl sulfoxide, sulfolane,  $\gamma$ -butyrolactone, and toluene. However, it should not be construed that the invention is limited thereto. These solvents may be used alone or in admixture.

The concentration of the foregoing components (the whole of solid contents including the additives) in the solvent is preferably from 1 to 50 % by mass.

[0179]

The coating amount (solids content) on the support obtained after coating and drying varies depending on the utility, but so far as image forming layers of planographic printing plate precursor are concerned, it is usually preferably from 0.5 to 5.0

g/m<sup>2</sup>. As the coating amount decreases, the apparent sensitivity increases, but film characteristics of the image forming layer are lowered.

[0180]

As the method of coating, various methods can be employed. Examples include bar coater coating, rotary coating, spray coating, curtain coating, dip coating, air knife coating, blade coating, and roll coating.

In the invention, surfactants for improving the coating property, such as fluorine based surfactants described in JP-A No. 62-170950, can be added to the image forming layer. The addition amount of such a surfactant is preferably from 0.01 to 1 % by mass, and more preferably from 0.05 to 0.5 % by mass in the whole of solid contents of the image forming layer.

[0181]

[Resin interlayer]

In the planographic printing plate precursor, it is possible to provide a resin interlayer between the image forming layer and the support, if desired.

By providing the resin interlayer, an infrared-sensitive layer (image recording layer) whose solubility in alkaline developing solutions increases upon exposure is provided on the exposure surface or in the vicinity thereof, whereby the sensitivity to infrared laser becomes better. Further, when a resin interlayer made of a high-molecular compound is provided between the

support and the infrared-sensitive layer, the resin interlayer functions as a heat insulating layer. Accordingly, there gives rise to an advantage such that a heat generated by exposure with infrared laser does not diffuse into the support but is efficiently used for image formation, thereby achieving high sensitivity. Further, in unexposed areas, the image recording layer that is non-penetrating against alkaline developing solutions functions itself as a protective layer of the resin interlayer. Accordingly, it is thought that not only development stability becomes good, but also images having excellent discrimination can be formed and that stability with time can be ensured. Additionally, the resin interlayer is preferably constituted as a layer made of an alkali-soluble high-molecular compound as the major component and is extremely good in solubility in developing solutions. Accordingly, by providing such a resin interlayer in the vicinity of the support, even in the case where a developing solution whose activity has been lowered is used, when the components of the photosensitive layer whose dissolution inhibiting ability has been released by exposure are dissolved and dispersed in the developing solution, exposed areas are rapidly removed without generation of film retention, and the like. It is thought that this also contributes to an improvement of developability. From the foregoing reasons, it is thought that the resin interlayer is useful.

[0182]

[Support]

The support that is used in the present invention is a dimensionally stable sheet-like material. Examples include papers, papers laminated with plastics (such as polyethylene, polypropylene, and polystyrene), metal sheets (such as aluminum, zinc, and copper), and plastic films (such as cellulose diacetate, cellulose triacetate, cellulose propionate, cellulose butyrate, cellulose acetate butyrate, cellulose nitrate, polyethylene terephthalate, polyethylene, polystyrene, polypropylene, polycarbonate, and polyvinyl acetal), and the foregoing papers or plastic films laminated or vapor deposited with metals.

In the case where the present invention is applied to a planographic printing plate precursor, polyester films or aluminum sheets are preferable as the support according to the invention. Of these, aluminum sheets that have good dimensional stability and are relatively cheap are particularly preferable. Suitable aluminum sheets are pure aluminum sheets and alloy sheets containing aluminum as a major component and trace amounts of foreign elements, and further, plastic films laminated or vapor deposited with aluminum may be employed. Examples of foreign elements contained in aluminum alloys include silicon, iron, manganese, copper, magnesium, chromium, zinc, bismuth, nickel, and titanium. The content of foreign elements in the alloy is at most 10 % by mass. In the invention, pure aluminum is particularly suitable. However, since it is difficult to produce completely pure aluminum from the standpoint of refining

technology, those containing slightly foreign elements may be used.

Aluminum sheets that are applied to the present invention are not specified with respect to their compositions, and those that have hitherto been known and used can be properly utilized. The aluminum sheets that are applied in the invention have a thickness of about 0.1 to 0.6 mm, preferably 0.15 to 0.4 mm, and particularly preferably 0.2 to 0.3 mm.

[0183]

Prior to roughing the aluminum sheet, if desired, the aluminum sheet is subjected to degreasing processing with, for example, a surfactant, an organic solvent or an alkaline aqueous solution for the purpose of removing a rolling oil on the surface. The roughing processing of the surface of the aluminum shesan be carried out by various methods such as a method of mechanically roughing the surface, a method of electrochemically dissolving and roughing the surface, and a method of chemically selectively dissolving the surface. As the mechanical method, known methods such as ball polishing, brush polishing, blast polishing, and buff polishing can be employed. As the electrochemical roughing method, a method of using an alternating current or direct current in a hydrochloric acid or nitric acid electrolytic solution can be employed. Further, a combination of the both methods as disclosed in JP-A No. 54-63902 can also be employed. The thus roughed aluminum sheet is subjected to alkali etching

processing and neutralization processing as the need arises. Thereafter, if desired, the aluminum sheet is further subjected to anodic oxidation processing for the purpose of enhancing water retention and ablation resistance of the surface. As electrolytes to be used for the anodic oxidation processing of the aluminum sheet, various electrolytes capable of forming a porous oxidized film can be used. In general, sulfuric acid, phosphoric acid, oxalic acid, chromic acid, or mixed acids thereof can be used. A concentration of such an electrolyte is properly determined depending on the kind of electrolyte.

[0184]

The processing condition of the anodic oxidation varies depending on the electrolyte and hence, cannot be unequivocally specified. In general, it is proper that: the concentration of electrolyte is from 1 to 80 % by mass, the liquid temperature is from 5 to 70 °C, the current density is from 5 to 60 A/dm<sup>2</sup>, the voltage is from 1 to 100 V, and the electrolysis time is from 10 seconds to 5 minutes. When the amount of the anodically oxidized film is less than 1.0 g/m<sup>2</sup>, press life is liable to be insufficient, or scuffs are likely formed in non-image areas of planographic printing plate, whereby so-called "scuff stain" in which an ink easily adheres to scuffs during printing is likely generated. After the anodic oxidation processing, the aluminum surface is subjected to hydrophilic processing. Examples of the hydrophilic processing that is used in the invention include a method of using

alkali metal silicates (such as a sodium silicate aqueous solution) as disclosed in USP Nos. 2,714,066, 3,181,461, 3,280,734, and 3,902,734. According to this method, the support is subjected to dip processing or electrolysis processing with a sodium silicate aqueous solution. Besides, there are employed a method of processing with potassium fluorozirconate as disclosed in JP-B No. 36-22063 and a method of processing with polyvinylphosphonic acid as disclosed in USP Nos. 3,276,868, 4,153,461 and 4,689,272.

[0185]

The planographic printing plate precursor to which the present invention is applied is one comprising a positive image forming layer provided on the support, and an undercoating layer can be provided therebetween as the need arises.

As components of the undercoating layer, various organic compounds are used. Examples include carboxymethyl cellulose; dextrin; gum arabic; amino group-containing phosphonic acids such as 2-aminoethylphosphonic acid; optionally substituted organic phosphonic acids such as phenylphosphonic acid, naphthylphosphonic acid, alkylphosphonic acids, glycerophosphonic acid, methylenediphosphonic acid, and ethylenediphosphonic acid; optionally substituted organic phosphoric acids such as phenylphosphoric acid, naphthylphosphoric acid, alkylphosphoric acids, and glycerophosphoric acid; optionally substituted organic phosphinic

acids such as phenylphosphinic acid, naphthylphosphinic acid, alkylphosphinic acids, and glycerophosphinic acid; amino acids such as glycine and  $\beta$ -alanine; and hydroxyl group-containing amino hydrochlorides such as triethanolamine hydrochloride.

These compounds may be used in admixture of two or more thereof.

[0186]

This organic undercoating layer can be provided in the following methods. That is, there are a method in which a solution of the organic compound dissolved in water or an organic solvent such as methanol, ethanol, and methyl ethyl ketone is coated on an aluminum sheet and dried to provide an organic undercoating layer; and a method in which an aluminum sheet is dipped in a solution of the organic compound dissolved in water or an organic solvent such as methanol, ethanol, and methyl ethyl ketone to adsorb the compound on the aluminum sheet, which is then rinsed with water, and the like, and dried to provide an organic undercoating layer. In the former method, a solution of the organic compound having a concentration of 0.005 to 10 % by mass can be coated in various methods.

In the latter method, the concentration of the solution is from 0.01 to 20 % by mass, and preferably from 0.05 to 5 % by mass; the dipping temperature is from 20 to 90 °C, and preferably from 25 to 50 °C; and the dipping time is from 0.1 seconds to 20 minutes, and preferably from 2 seconds to one minute. It is

possible to adjust the solution as used herein so as to have a pH in the range of 1 to 12 with basic substances such as ammonia, triethylamine, and potassium hydroxide, or acidic substances such as hydrochloric acid and phosphoric acid. For improving tone reproducibility of image recording materials, yellow dyes may be added.

A coverage of the organic undercoating layer is suitably from 2 to 200 mg/m<sup>2</sup>, and preferably from 5 to 100 mg/m<sup>2</sup>. When the coverage is less than 2 mg/m<sup>2</sup>, sufficient press life cannot be obtained. When it exceeds 200 mg/m<sup>2</sup>, sufficient press life cannot be obtained, too.

[0187]

[Exposure and development]

The thus prepared positive planographic printing plate precursor is usually imagewise exposed and then developed.

As light sources of rays to be used for imagewise exposure, light sources having an light-emitting wavelength in near infrared to infrared revisions are preferable, and solid lasers and semiconductor lasers are particularly preferable.

[0188]

As the developing solution and a replenisher thereof of the planographic printing plate precursor to which the image forming material of the invention is applied, conventionally known alkaline aqueous solutions can be used.

Examples include inorganic alkali salts such as sodium

silicate, potassium silicate, sodium tertiary phosphate, potassium tertiary phosphate, ammonium tertiary phosphate, sodium secondary phosphate, potassium secondary phosphate, ammonium secondary phosphate, sodium carbonate, potassium carbonate, ammonium carbonate, sodium hydrogencarbonate, potassium hydrogencarbonate, ammonium hydrogencarbonate, sodium borate, potassium borate, ammonium borate, sodium hydroxide, ammonium hydroxide, potassium hydroxide, and lithium hydroxide; and organic alkaline agents such as monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monoisopropylamine, diisopropylamine, triisopropylamine, n-butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, ethyleneimine, ethylenediamine, and pyridine. These alkaline agents may be used alone or in combination of two or more thereof.

Of these alkaline developing solutions are particularly preferable aqueous solutions of silicates such as sodium silicate and potassium silicate. This is because it is possible to adjust the developability by a ratio of silicon oxide  $\text{SiO}_2$  as the component of the silicate to an alkali metal oxide  $\text{M}_2\text{O}$  and a concentration thereof. For example, alkali metal silicates described in JP-A No. 54-62004 and JP-B No. 57-7427 are effectively used.

[0189]

In addition, in the case where development is carried out

using an automatic processor, it is known that by adding one the same as in the developing solution or an aqueous solution (replenisher) having a higher alkaline strength than the developing solution to the developing solution, a large amount of planographic printing plate precursors can be processed without exchanging the developing solution as used in a developing bath over a long period of time. This method is suitably applied, too in the present invention.

[0190]

For the purposes of accelerating or retarding developability, diffusing development scums, and enhancing ink-philic property of image areas of printing plates, various surfactants and organic solvents can be added to the developing solution and replenisher, as the need arises.

As surfactants are preferable anionic, cationic, nonionic and amphotolytic surfactants. Also, it is possible to add hydroquinone, resorcin, inorganic salt based reducing agents such as sodium salts and potassium salts of inorganic acids such as sulfurous acid and hydrogensulfurous acid, organic carboxylic acids, defoaming agent, or hard water softeners to the developing solution and replenisher, as the need arises.

The printing plate thus developed using the developing solution and replenisher is subjected to post treatment with, for example, washing water, a rinse solution containing a surfactant, and a desensitizing solution containing gum arabic and starch

derivatives. In the invention, in the case where the image forming material is used as a printing plate, these treatments can be employed through various combinations as the post treatment.

[0191]

In recent years, in the industries of plate making and printing, for the purposes of rationalization and standardization, an automatic processor for printing plate is widely used. Such an automatic processor generally includes a development section and a post treatment section and further includes a unit for conveying a printing plate and respective processing solution tanks and spray units, in which an exposed printed plate is conveyed horizontally and developed while spraying each of processing solutions drawn up by a pump from spray nozzles. Further, recently, there is also known a method in which a printing plate is processed in a processing solution tank filled with a processing solution while dipping and conveying by guide rollers. In such automatic processing, the processing can be performed while replenishing a replenisher to each processing solution according to the processing amount and operation time. Moreover, a so-called non-returnable processing system of treating with a substantially virgin processing solution can also be applied.

[0192]

In the present invention, in the case where a planographic printing plate obtained by imagewise exposing, developing and water washing and/or rinsing and/or gumming includes

unnecessary image areas (for example, film edge marks of original image film), the unnecessary image areas are erased. For achieving erosion, it is preferred to employ a method in which an erasing solution described in JP-B No. 2-13293 is coated on unnecessary image areas, and the coated unnecessary image areas are allowed to stand for a while as they are and then washed with water. Also, there can be utilized a method in which unnecessary image areas are irradiated with actinic rays introduced through an optical fiber and then developed described in JP-A No. 59-174842.

[0193]

The thus obtained planographic printing plate can be provided for printing step after coating a desensitizing gum, if desired. In the case where a planographic printing plate is required to have higher press life, the planographic printing plate is subjected to burning processing. In the case where a planographic printing plate is subjected to burning processing, it is preferred to treat the planographic printing plate with a surface conditioning solution described in JP-B Nos. 61-2518 and 55-28062, JP-A Nos. 62-31859 and 61-159655 prior to the burning processing.

Examples of methods of performing such processing include a method in which a surface conditioning solution is coated on a planographic printing plate using a sponge or absorbent cotton impregnated with the surface conditioning

solution, a method in which the planographic printing plate is dipped in a vat filled with a surface conditioning solution and coated with the surface conditioning solution, and a method in which a surface conditioning solution is coated using an automated coater. Further, what a coating amount is made uniform after coating by a squeegee or a squeegee roller gives rise more preferred results.

[0194]

A suitable coating amount of the surface conditioning solution is in general from 0.03 to 0.8 g/m<sup>2</sup> (on a dry mass). The surface conditioning solution-coated planographic printing plate is heated at high temperatures by a burning processor (for example, a burning processor "BP-1300" (trade name) sold by Fuji Photo Film Co., Ltd.), and the like after drying, as the need arises. In this case, the heating temperature and time vary depending on the kind of components forming an image, and the heating is preferably carried out at from 180 to 300 °C for from 1 to 20 minutes.

[0195]

If desired, the burning processed planographic printing plate can be properly subjected to conventionally employed processings such as water washing and gumming. In the case where a surface conditioning solution containing a water-soluble high-molecular compound is used, so-called desensitizing processing such as gumming can be omitted. The planographic

printing plate thus obtained through such processings is fixed in an offset printer and used for producing a number of prints.

[0196]

[EXAMPLES]

The present invention will be described below with reference to the following Examples, but it should not be construed that the invention is limited thereto.

[0197]

[Preparation of substrate A]

A 0.24 mm-thick aluminum plate (an aluminum alloy containing 0.06 % by mass of Si, 0.30 % by mass of Fe, 0.014 % by mass of Cu, 0.001 % by mass of Mn, 0.001 % by mass of Mg, 0.001 % by mass of Zn, and 0.03 % by mass of Ti, with the remainder being Al and inevitable impurities) was subjected continuously to the following processings.

[0198]

The aluminum plate was subjected to continuous electrochemical roughing processing using an alternating current of 60 Hz. At this time, an electrolytic solution that was used was an aqueous solution of 10 g/L of nitric acid (containing 5 g/L of aluminum ions and 0.007 % by mass of ammonium ions) at a temperature of 80 °C. After washing with water, the aluminum plate was subjected to etching processing at 32 °C by spraying a solution having a sodium hydroxide concentration of 26 % by mass and an aluminum ion concentration of 6.5 % by mass to

dissolve 0.20 g/m<sup>2</sup> of the aluminum plate, followed by washing with water by spraying. Thereafter, the aluminum plate was subjected to desmutting processing by spraying an aqueous solution having a sulfuric acid concentration of 25 % by mass (containing 0.5 % by mass of aluminum ions) at a temperature of 60 °C and washed with water by spraying.

[0199]

The aluminum plate was subjected to anodic oxidation processing using an anodic oxidation system by two-stage feeding electrolysis processing. Sulfuric acid was used as an electrolytic solution to be supplied in an electrolysis section. Thereafter, the aluminum plate was washed with water by spraying. A final amount of oxidized film was 2.7 g/m<sup>2</sup>.

The aluminum support obtained by anodic oxidation processing was treated with an alkali metal silicate (silicate processing) by dipping in a processing bath containing a 1 % by mass aqueous solution of No. 3 sodium silicate at a temperature of 30 °C for 10 seconds. Thereafter, the aluminum support was washed with water by spraying.

[0200]

An undercoating solution having the following composition was coated on the thus obtained aluminum support after treatment with an alkali metal silicate and dried at 80 °C for 15 seconds to form a coating film, whereby a substrate A was

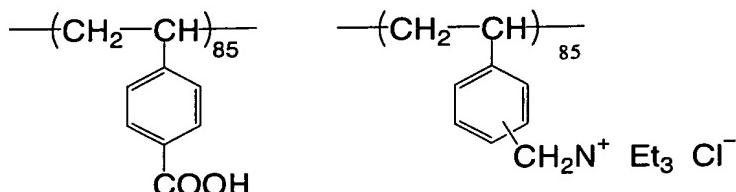
obtained. After drying, the coating film had a coverage of 15 mg/m<sup>2</sup>.

[0201]

<Composition of undercoating solution>

- Compound as shown below: 0.3 g
- Methanol: 100 g
- Water: 1 g

[0202]



Molecular weight: 28,000

[0203]

[Preparation of substrate B]

A 0.24 mm-thick aluminum plate (an aluminum alloy containing 0.06 % by mass of Si, 0.30 % by mass of Fe, 0.014 % by mass of Cu, 0.001 % by mass of Mn, 0.001 % by mass of Mg, 0.001 % by mass of Zn, and 0.03 % by mass of Ti, with the remainder being Al and inevitable impurities) was subjected continuously to the following processings.

[0204]

The surface of the aluminum plate was mechanically roughed using a rotating roller-shaped nylon brush while supplying a suspension of a polishing agent (quartz sand) and

water with a specific gravity of 1.12 as a polishing slurry liquid. Thereafter, the aluminum plate was subjected to etching processing at 70 °C by spraying a solution having a sodium hydroxide concentration of 2.6 % by mass and an aluminum ion concentration of 6.5 % by mass to dissolve 6 g/m<sup>2</sup> of the aluminum plate, followed by washing with water by spraying. Further, the aluminum plate was subjected to desmutting processing by spraying an aqueous solution having a nitric acid concentration of 1 % by mass (containing 0.5 % by mass of aluminum ions) at a temperature of 30 °C and washed with water by spraying. Thereafter, the aluminum plate was subjected to continuous electrochemical roughing processing using an alternating current of 60 Hz. At this time, an electrolytic solution was an aqueous solution of 10 g/L of nitric acid (containing 5 g/L of aluminum ions and 0.007 % by mass of ammonium ions) at a temperature of 80 °C. After washing with water, the aluminum plate was subjected to etching processing at 32 °C by spraying a solution having a sodium hydroxide concentration of 26 % by mass and an aluminum ions concentration of 6.5 % by mass to dissolve 0.20 g/m<sup>2</sup> of the aluminum plate, followed by washing with water by spraying. Thereafter, the aluminum plate was subjected to desmutting processing by spraying an aqueous solution having a sulfuric acid concentration of 25 % by mass (containing 0.5 % by mass of aluminum ions) at a temperature of 60 °C and washed with water by spraying.

[0205]

The aluminum plate was subjected to anodic oxidation processing using an anodic oxidation system by two-stage feeding electrolysis processing. Sulfuric acid was used as an electrolytic solution to be supplied in an electrolysis section. Thereafter, the aluminum plate was washed with water by spraying. A final amount of oxidized film was 2.7 g/m<sup>2</sup>.

The aluminum support obtained by anodic oxidation processing was treated with an alkali metal silicate (silicate processing) by dipping in a processing bath containing a 1 % by mass aqueous solution of No. 3 sodium silicate at a temperature of 30 °C for 10 seconds. Thereafter, the aluminum support was washed with water by spraying.

[0206]

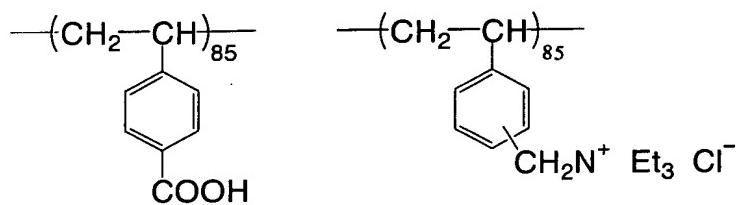
An undercoating solution having the following composition was coated on the thus obtained aluminum support after treatment with an alkali metal silicate and dried at 80 °C for 15 seconds to form a coating film, whereby a substrate B was obtained. After drying, the coating film had a coverage of 15 mg/m<sup>2</sup>.

[0207]

<Composition of undercoating solution>

- |                            |       |
|----------------------------|-------|
| • Compound as shown below: | 0.3 g |
| • Methanol:                | 100 g |
| • Water:                   | 1 g   |

[0208]



Molecular weight: 28,000

[0209]

[Synthesis of copolymer]

In a 500-mL three-necked flask equipped with a stirrer, a condenser and a dropping funnel, 31.0 g (0.36 moles) of methacrylic acid, 39.1 g (0.36 moles) of ethyl chloroformate, and 200 mL of acetonitrile were charged, and the mixture was stirred while being cooled in an ice water bath. To this mixture, 36.4 g (0.36 moles) of triethylamine was added dropwise from the dropping funnel over about 1 hour. After completion of the dropwise addition, the ice water bath was removed, and the resulting mixture was stirred at room temperature for 30 minutes.

[0210]

To the reaction mixture, 51.7 g (0.30 moles) of p-aminobenzenesulfonamide was added, and the mixture was stirred for 1 hour while being warmed it at 70 °C in an oil bath. After completion of the reaction, the mixture was added to one liter of water while the water was stirred, and the resulting mixture was stirred for 30 minutes. The mixture was subjected to filtration, and deposits were taken out and formed into a slurry with 500 mL

of water. The slurry was subjected to filtration, and the resulting solid was dried to obtain a white solid of N-(p-aminosulfonylphenyl)methacrylamide (yield: 46.9 g).

[0211]

Next, 4.61 g (0.0192 moles) of N-(p-aminosulfonylphenyl)-methacrylamide, 2.58 g (0.0258 moles) of ethyl methacrylate, 0.80 g (0.015 moles) of acrylonitrile, and 20g of N,N-dimethylacetamide were charged in a 200-mL three-necked flask equipped with a stirrer, a condenser and a dropping funnel, and the mixture was stirred while being heated at 65 °C in a warm water bath. To this mixture, 0.15 g of 2,2'-azobis(2,4-dimethylvaleronitrile) (a trade name: V-65, manufactured by Wako Pure Chemical Industries, Ltd.) was added as a polymerization initiator, and the mixture was stirred under a nitrogen gas stream for 2 hours while being kept it at 65 °C. A mixture of 4.61 g of N-(p-aminosulfonyl-phenyl)methacrylamide, 2.58 g of methyl methacrylate, 0.80 g of acrylonitrile, 20 g of N,N-dimethylacetamide, and 0.15 g of the aforementioned V-65 was further added dropwise to the reaction mixture from the dropping funnel over 2 hours. After completion of the dropwise addition, the resulting mixture was stirred at 65 °C for an additional 2 hours. After completion of the reaction, 40 g of methanol was added to the reaction mixture, and the mixture was cooled. The resulting mixture was added to two liters of water while the water was stirred, and the mixture was stirred for 30 minutes. Deposits were taken out by filtration and dried to obtain

15 g of a white solid. This copolymer was measured by gel permeation chromatography and found to have a weight average molecular weight (polystyrene standard) of 54,000.

[0212]

(Examples 1 to 8)

[Preparation of planographic printing plate precursor]

On the obtained substrate A, the following coating solution 1 for an mage forming layer was coated in a coating amount of 0.85 g/m<sup>2</sup> and dried at 110 °C for 50 seconds by a PERFECT OVEN PH200 (manufactured by TABAI ESPEC CORP.) while the wind control set at 7. Thereafter, the following coating solution 2 for an image forming layer was coated in a coating amount of 0.30 g/m<sup>2</sup> and then dried at 120 °C for one minute, whereby planographic printing plate precursors were obtained.

[0213]

<Coating solution 1 for image forming layer>

• Copolymer as described above:	2.133 g
• Specific IR coloring material shown in Table 15:	0.109 g
• 4,4'-Bishydroxyphenylsulfone:	0.126 g
• Cis-Δ <sup>4</sup> -tetrahydronaphthalic anhydride:	0.190 g
• p-Toluenesulfonic acid:	0.008 g
• 3-Methoxy-4-diazodiphenylamine hexafluoro-phosphate:	0.030 g
• Ethyl Violet whose counter ion is changed to an anion of 6-hydroxy-2-naphthalenesulfonic acid:	0.100 g

- MEGAFAC F-176 (a trade name for surface property improving fluorine based surfactant, manufactured by Dainippon Ink and Chemicals, Incorporated): 0.035 g
- Methyl ethyl ketone: 25.38 g
- 1-Methoxy-2-propanol: 13.0 g
- $\gamma$ -Butyrolactone: 13.2 g

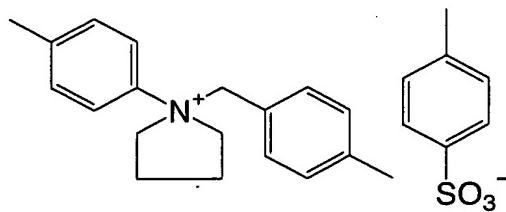
[0214]

<Coating solution 2 for image forming layer>

- m,p-Cresol novolac (m/p ratio: 6/4, weight average molecular weight: 4,500, containing 0.8 % by weight of unreacted cresols): 0.3478 g
- Specific IR coloring material shown in Table 15: 0.011 g
- Ethyl Violet whose counter ion is changed to 6-hydroxy-2-naphthalenesulfonic acid: 0.010 g
- Ammonium salt compound (1) having a structure as shown below: 0.010 g
- MEGAFAC F-176 (20 %) (a trade name for surface property improving surfactant, manufactured by Dainippon Ink and Chemicals, Incorporated): 0.022 g
- Methyl ethyl ketone: 13.07 g
- 1-Methoxy-2-propanol: 6.79 g

[0215]

Ammonium salt compound (1)



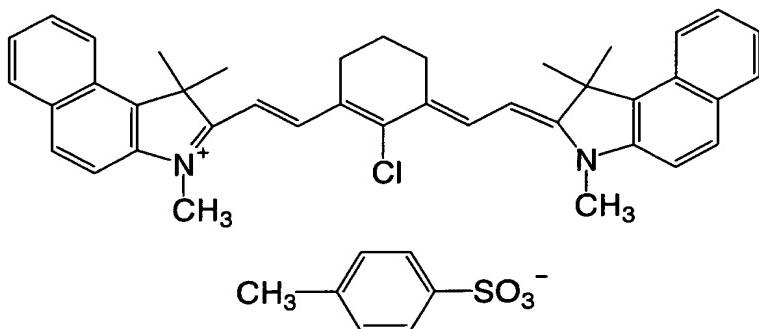
[0216]

(Comparative Example 1)

A planographic printing plate precursor was obtained in the same manner as in the foregoing Examples 1 to 8, except for using coating solutions prepared by adding a cyanine dye CD-X having the following structure in place of the specific IR coloring materials shown in Table 15 in the coating solutions 1 and 2 for image forming layer.

[0217]

Cyanine dye CD-X



[0218]

[Evaluation of planographic printing plate precursor]

Each of the thus obtained planographic printing plate precursors was evaluated using the following method. The evaluation results are also shown in Table 15.

(Sensitivity)

The obtained planographic printing plate precursor had a solid image drawn thereon using a TRENDSETTER (a trade name, manufactured by Creo Inc.) at a beam strength in the range of from 2 to 10 W and at a drum rotation speed of 150 rpm and was then developed for 12 seconds using a PS processor, LP940H (a trade name, manufactured by Fuji Photo Film Co., Ltd.) charged with a developing solution, DT-2 (a trade name, manufactured by Fuji Photo Film Co., Ltd.), (diluted at 1/8) and a finisher, FG-1 (a trade name, manufactured by Fuji Photo Film Co., Ltd.), (diluted at 1/1) while keeping a liquid temperature at 30 °C. At this time, the developing solution had a conductivity of 43 mS/cm.

After the development, the printing plate precursor was observed with a loupe with a magnification of 25 times, and the presence or absence of film retention at a level at which printing staining did not substantially occur was evaluated. Then, an actual exposure energy was calculated from an exposure beam intensity at which no film retention was observed and defined as a sensitivity. According to the evaluation, the smaller the exposure energy is, the higher the sensitivity is.

[0219]

(Development latitude)

The obtained planographic printing plate precursor had a test pattern thereon using a TRENDSETTER (a trade name, manufactured by Creo Inc.) at a beam strength of 9 W and at a drum rotation speed of 150 rpm and was then developed for 12 seconds using a PS processor, LP940H (a trade name, manufactured by Fuji Photo Film Co., Ltd.), charged with a solution obtained by diluting a developing solution, DT-2R (a trade name, manufactured by Fuji Photo Film Co., Ltd.), at 1/5 and blowing a carbon dioxide gas thereinto until the conductivity reached 37 mS/cm and a finisher, FG-1 (a trade name, manufactured by Fuji Photo Film Co., Ltd.), (diluted at 1/1) while keeping a liquid temperature at 30 °C. Thereafter, a suitable amount of DT-2R (diluted at 1/5) was added to the developing solution to adjust the conductivity to 39 mS/cm, and a planographic printing plate precursor on which a test pattern had been similarly imagewise drawn was developed. Further, the conductivity was increased by 2 mS/cm at a time, and this operation was continued until film diminishment due to development of the image was significantly observed.

At this time, the presence or absence of staining or coloration caused by film retention of the image forming layer due to development failure was confirmed for the printing plate developed at each of the conductivities, and a conductivity of the

developing solution at which the development could be performed well was determined. Next, a critical conductivity at which the development film diminishment was kept at a level such that printing resistance was not substantially influenced was determined.

A range between the conductivity of the developing solution at which the development could be performed well and the critical conductivity at which the development film diminishment was kept at a level such that printing resistance was not substantially influenced was defined as development latitude.

Incidentally, the wider the range of development latitude is, the larger the difference between solubilities in developing solutions at exposed areas and unexposed areas (solubility discrimination) which is one of the effects of the present invention.

[0220]

[Table 15]

	Specific IR coloring material (Coating solution 1 for image forming layer)	Specific IR coloring material (Coating solution 2 for image forming layer)	Sensitivity (mJ/cm <sup>2</sup> )	Development latitude (mS/cm)
Example 1	CD-1	CD-1	105	10
Example 2	CD-10	CD-10	100	10
Example 3	CD-27	CD-27	100	10
Example 4	CD-38	CD-38	105	12
Example 5	CD-50	CD-50	105	10
Example 6	PD-3	PD-3	110	12
Example 7	PD-19	PD-19	110	10
Example 8	AD-2	AD-2	110	12
Comparative Example 1	CD-X *	CD-X *	135	8

\*: A general cyanine dye CD-X was used in place of the specific IR coloring material according to the present invention.

[0221]

As is clear from Table 15, it was confirmed that the planographic printing plate precursors of Examples 1 to 8 using the specific IR coloring material according to the present invention can achieve high sensitivity together with a wide development latitude better than the planographic printing plate precursor of Comparative Example 1 having a generally widely employed cyanine dye CD-X added thereto.

[0222]

(Examples 9 to 16)

[Preparation of planographic printing plate precursor]

On the substrate A, the following coating solution 3 for an image forming layer was coated in a coating amount of 1.00 g/m<sup>2</sup> and dried at 110 °C for 50 seconds by a PERFECT OVEN PH200 (manufactured by TABAI ESPEC CORP.) with the wind control set at 7. Thereafter, the following coating solution 4 for an image forming layer was coated in a coating amount of 0.24 g/m<sup>2</sup> and then dried at 120 °C for one minute, whereby planographic printing plate precursors were obtained.

[0223]

<Coating solution 3 for image forming layer>

• Copolymer as described above:	2.133 g
• Specific IR coloring material shown in Table 16:	0.109 g
• 4,4'-Bishydroxyphenylsulfone:	0.125 g
• Cis-Δ <sup>4</sup> -tetrahydronaphthalic anhydride:	0.190 g
• p-Toluenesulfonic acid:	0.008 g
• 3-Methoxy-4-diazodiphenylamine hexafluorophosphate:	0.030 g
• Ethyl Violet whose counter ion is changed to an anion of 6-hydroxy-2-naphthalenesulfonic acid:	0.100 g
• MEGAFAC F-176 (a trade name for surface property improving fluorine based surfactant, manufactured by Dainippon Ink and Chemicals, Incorporated):	0.035 g
• Methyl ethyl ketone:	25.38 g
• 1-Methoxy-2-propanol:	13.0 g
• γ-Butyrolactone:	13.2 g

[0224]

<Coating solution 4 for image forming layer>

- m,p-Cresol novolac 0.320 g  
(m/p ratio: 6/4, weight average molecular weight: 4,500, containing 0.8 % by weight of unreacted cresols):
- Specific IR coloring material shown in Table 16: 0.010 g
- Copolymer of ethyl methacrylate and 0.030 g  
2-methacryloyloxyethyl succinic acid  
(molar ratio: 67/33, weight average molecular weight: 92,000):
- Ethyl Violet whose counter ion is changed to 0.012 g  
6-hydroxy-2-naphthalenesulfonic acid:
- MEGAFAC F-176 (20 %) 0.022 g  
(a trade name for surface property improving surfactant, manufactured by Dainippon Ink and Chemicals, Incorporated):
- Methyl ethyl ketone: 13.07 g
- 1-Methoxy-2-propanol: 6.79 g

[0225]

(Comparative Example 2)

A planographic printing plate precursor was obtained in the same manner as in the foregoing examples 9 to 16, except for using coating solutions prepared by adding the cyanine dye CD-X described in comparative example 1 in place of the specific IR coloring materials shown in Table 16 in the coating solutions 3 and 4 for image forming layer.

[0226]

[Evaluation of planographic printing plate precursor]

Each of the thus obtained planographic printing plate precursors was evaluated with respect to the sensitivity and development latitude in the same manners as in Examples 1 to 8.

The evaluation results are also shown in Table 16.

[0227]

[Table 16]

	Specific IR coloring material (Coating solution 3 for image forming layer)	Specific IR coloring material (Coating solution 4 for image forming layer)	Sensitivity (mJ/cm <sup>2</sup> )	Development latitude (mS/cm)
Example 9	CD-2	CD-2	95	10
Example 10	CD-17	CD-17	95	10
Example 11	CD-29	CD-29	90	10
Example 12	CD-36	CD-36	95	12
Example 13	CD-3	CD-54	95	10
Example 14	CD-1	PD-1	100	12
Example 15	PD-2	PD-22	105	10
Example 16	AD-6	CD-27	105	12
Comparative Example 2	CD-X *	CD-X *	125	8

\*: A general cyanine dye CD-X was used in place of the specific IR coloring material according to the invention.

[0228]

As is clear from Table 16, it was confirmed that the planographic printing plate precursors of Examples 9 to 16 using the specific IR coloring material according to the invention can achieve high sensitivity together with a wide development latitude better than the planographic printing plate precursor of

Comparative Example 2 having a generally widely employed cyanine dye CD-X added thereto.

[0229]

(Examples 17 to 24)

[Preparation of planographic printing plate precursor]

On the substrate B, the following coating solution 5 for an image forming layer was coated in a coating amount of 1.00 g/m<sup>2</sup> and dried at 110 °C for 50 seconds by a PERFECT OVEN PH200 (manufactured by TABAI ESPEC CORP.) with the wind control set at 7. Thereafter, the following coating solution 6 for an image forming layer was coated in a coating amount of 0.30 g/m<sup>2</sup> and then dried at 120 °C for one minute, whereby planographic printing plate precursors were obtained.

[0230]

<Coating solution 5 for image forming layer>

- Copolymer as described above: 2.133 g
- Specific IR coloring material shown in Table 17: 0.109 g
- 2-Mercapto-5-methylthio-1,3,4-thiadiazole: 0.120 g
- 4,4'-Bishydroxyphenylsulfone: 0.075 g
- Cis-Δ<sup>4</sup>-tetrahydronaphthalic anhydride: 0.120 g
- p-Toluenesulfonic acid: 0.008 g
- 3-Methoxy-4-diazodiphenylamine hexafluoro-phosphate: 0.030 g
- Victoria Pure Blue whose counter ion is changed to an anion of 6-hydroxy-2-naphthalenesulfonic acid: 0.100 g

• MEGAFAC F-176 (a trade name for surface property improving fluorine based surfactant, manufactured by Dainippon Ink and Chemicals, Incorporated):	0.035 g
• Methyl ethyl ketone:	25.38 g
• 1-Methoxy-2-propanol:	13.0 g
• $\gamma$ -Butyrolactone:	13.2 g

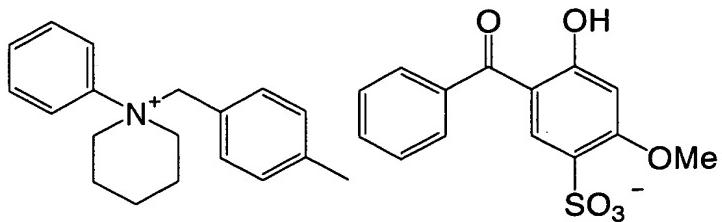
[0231]

<Coating solution 6 for image forming layer>

• m,p-Cresol novolac (m/p ratio: 6/4, weight average molecular weight: 4,500, containing 0.8 % by weight of unreacted cresols):	0.320 g
• Specific IR coloring material shown in Table 22:	0.0120 g
• Ethyl Violet whose counter ion is changed to an anion of 6-hydroxy-2-naphthalenesulfonic acid:	0.030 g
• Copolymer of ethyl methacrylate and 2-methacryloyloxyethyl succinic acid (molar ratio: 67/33, weight average molecular weight: 92,000):	0.030 g
• Ammonium salt compound (2) having a structure as shown below:	0.0080 g
• MEGAFAC F-176 (20 %) (a trade name for surface property improving surfactant, manufactured by Dainippon Ink and Chemicals, Incorporated):	0.022 g
• Methyl ethyl ketone:	13.07 g
• 1-Methoxy-2-propanol:	6.79 g

[0232]

Ammonium salt compound (2)



[0233]

(Comparative Example 3)

A planographic printing plate precursor was obtained in the same manner as in the foregoing Examples 17 to 24, except for using coating solutions prepared by adding the cyanine dye CD-X described in Comparative Example 1 in place of the specific IR coloring materials shown in Table 17 in the coating solutions 5 and 6 for image forming layer.

[0234]

[Evaluation of planographic printing plate precursor]

Each of the thus obtained planographic printing plate precursors was evaluated with respect to the sensitivity and development latitude in the same manners as in Examples 1 to 8. The evaluation results are also shown in Table 17.

[0235]

[Table 17]

	Specific IR coloring material (Coating solution 5 for image forming layer)	Specific IR coloring material (Coating solution 6 for image forming layer)	Sensitivity (mJ/cm <sup>2</sup> )	Development latitude (mS/cm)
Example 17	CD-5	CD-5	85	10
Example 18	CD-16	CD-16	80	10
Example 19	CD-20	CD-27	80	10
Example 20	CD-38	CD-60	85	12
Example 21	CD-50	CD-X	100	10
Example 22	CD-8	PD-3	90	12
Example 23	CD-22	PD-6	85	10
Example 24	CD-2	AD-12	85	12
Comparative Example 3	CD-X *	CD-X *	115	8

\*: A general cyanine dye CD-X was used in place of the specific IR coloring material according to the invention.

[0236]

As is clear from Table 17, it was confirmed that the planographic printing plate precursors of Examples 17 to 24 using the specific IR coloring material according to the present invention can achieve high sensitivity together with a wide development latitude better than the planographic printing plate precursor of Comparative Example 3 having a generally widely employed cyanine dye CD-X added thereto.

[0237]

(Examples 25 to 32)

[Preparation of planographic printing plate precursor]

On the substrate B, the following coating solution 7 for an image forming layer was coated in a coating amount after drying of

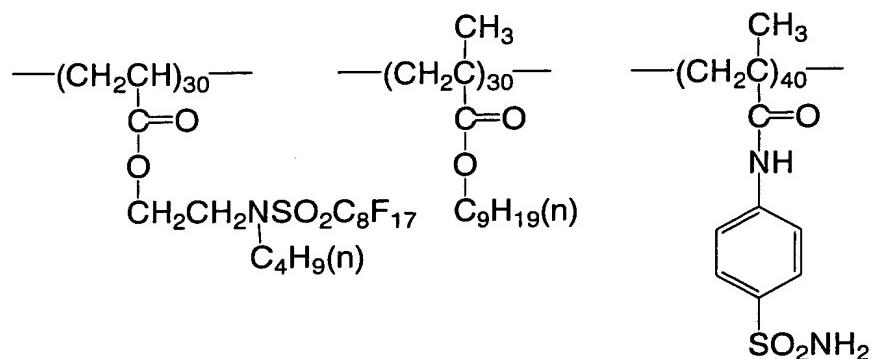
1.2 g/m<sup>2</sup>, whereby planographic printing plate precursors were obtained.

<Coating solution 7 for image forming layer>

- Fluorine-containing polymer (having a structure as shown below): 0.03 g
- Copolymer as described above: 0.75 g
- Novolac (m/p = 6/4, Mw = 4,000): 0.20 g
- Tetrapropylammonium p-hydroxybenzenesulfonate: 0.04 g
- Cis-Δ<sup>4</sup>-tetrahydronaphthalic anhydride: 0.03 g
- Specific IR coloring material shown in Table 18: 0.023 g
- Dye in which a counter ion of Victoria Pure Blue BOH is a 1-naphthalenesulfonic acid anion: 0.015 g
- 3-Methoxy-4-diazodiphenylamine hexafluoro-phosphate: 0.02 g
- n-Dodecyl stearate: 0.03 g
- Fluorine based surfactant (MEGAFAC F-177 (a trade name), manufactured by Dainippon Ink and Chemicals, Incorporated): 0.05 g
- γ-Butyrolactone: 10 g
- Methyl ethyl ketone: 10 g
- 1-Methoxy-2-propanol: 8 g

[0238]

Fluorine-containing polymer



[0239]

(Comparative Example 4)

A planographic printing plate precursor was obtained in the same manner as in the foregoing Examples 25 to 32, except for using coating solutions prepared by adding the cyanine dye CD-X described in Comparative Example 1 in place of the specific IR coloring materials shown in Table 18 in the coating solution 7 for image forming layer.

[0240]

[Evaluation of planographic printing plate precursor]

Each of the thus obtained planographic printing plate precursors was evaluated with respect to the sensitivity and development latitude in the same manners as in Examples 1 to 8. The evaluation results are also shown in Table 18.

[0241]

[Table 18]

	Specific IR coloring material (Coating solution 7 for image forming layer)	Sensitivity (mJ/cm <sup>2</sup> )	Development latitude (mS/cm)
Example 25	CD-4	75	8
Example 26	CD-11	75	8
Example 27	CD-30	80	8
Example 28	CD-41	75	8
Example 29	CD-56	75	10
Example 30	PD-10	80	8
Example 31	PD-24	80	8
Example 32	AD-13	80	8
Comparative Example 4	CD-X *	105	6

\*: A general cyanine dye CD-X was used in place of the specific IR coloring material according to the invention.

[0242]

As is clear from Table 18, it was confirmed that the planographic printing plate precursors of Examples 25 to 32 using the specific IR coloring material according to the invention can achieve a high sensitivity together with a wide development latitude better than the planographic printing plate precursor of Comparative Example 4 having a generally widely employed cyanine dye CD-X added thereto.

[0243]

(Examples 33 to 40)

[Preparation of planographic printing plate precursor]

On the substrate B, the following coating solution 8 for an image forming layer was coated and dried at 130 °C for 1 minute to

form an image forming layer, whereby planographic printing plate precursors were obtained. The coating amount after drying was 1.3 g/m<sup>2</sup>.

<Coating solution 8 for image forming layer>

- Novolac resin 1.0 g  
(Cresol novolac of m/p ratio = 6/4, Mw = 4,000):
- Copolymer of ethyl methacrylate and 0.10 g  
2-methacryloyloxyethyl succinic acid  
(molar ratio: 67/33, weight average molecular weight: 92,000):
- 2-Mercapto benzimidazole: 0.05 g
- Specific IR coloring material shown in Table 19: 0.05 g
- Dye in which a counter anion of Victoria Pure Blue BOH is a 6-hydroxy-2-naphthalenesulfonic acid anion: 0.01 g
- Fluorine based surfactant 0.05 g  
(MEGAFAC F-177 (a trade name), manufactured by Dainippon Ink and Chemicals, Incorporated):
- $\gamma$ -Butyrolactone: 3.0 g
- Methyl ethyl ketone: 8.0 g
- 1-Methoxy-2-propanol: 7.0 g

[0244]

(Comparative Example 5)

A planographic printing plate precursor was obtained in the same manner as in the foregoing Examples 33 to 40, except for using coating solutions prepared by adding the cyanine dye CD-X described in Comparative Example 1 in place of the specific IR

coloring materials shown in Table 19 in the coating solution 8 for image forming layer.

[0245]

[Evaluation of planographic printing plate precursor]

Each of the thus obtained planographic printing plate precursors was evaluated with respect to the sensitivity and development latitude in the same manners as in Examples 1 to 8.

The evaluation results are also shown in Table 19.

[0246]

[Table 19]

	Specific IR coloring material (Coating solution 8 for image forming layer)	Sensitivity (mJ/cm <sup>2</sup> )	Development latitude (mS/cm)
Example 33	CD-2	95	10
Example 34	CD-10	100	10
Example 35	CD-27	95	10
Example 36	CD-38	100	12
Example 37	CD-50	100	12
Example 38	PD-3	105	10
Example 39	PD-19	105	10
Example 40	AD-2	105	10
Comparative Example 5	CD-X *	125	6

\*: A general cyanine dye CD-X was used in place of the specific IR coloring material according to the invention.

[0247]

As is clear from Table 19, it was confirmed that the planographic printing plate precursors of Examples 33 to 40 using the specific IR coloring material according to the invention can

achieve high sensitivity together with a wide development latitude better than the planographic printing plate precursor of Comparative Example 5 having a generally widely employed cyanine dye CD-X added thereto.

[0248]

As shown in the aforementioned Examples, any of the planographic printing plate precursors using the specific IR coloring material according to the invention are excellent in sensitivity and solubility discrimination. Accordingly, it has been understood that the image forming material of the invention is useful as a heat mode-corresponding positive working planographic printing plate precursor.

[0249]

[Effects of the Invention]

According to the present invention, it is possible to provide an image forming material useful as a heat mode-corresponding positive working planographic printing plate precursor having a large difference of solubility in developing solutions between exposed areas and unexposed areas (solubility discrimination) and a high sensitivity.

[DOCUMENT NAME] ABSTRACT OF THE DISCLOSURE

[SUMMARY]

[OBJECT]

To provide an image forming material useful as a heat mode-corresponding positive working planographic printing plate precursor having a large difference of solubility in developing solutions between exposed areas and unexposed areas (solubility discrimination) and a high sensitivity.

[MEANS FOR SOLUTION]

An image forming material comprising a support and an image forming layer which is laminated on the support and contains at least (A) a water-insoluble and alkali-soluble high-molecular compound and (B) a compound having a structure represented by the following general formula (1) and having an absorption maximum at a wavelength in a range of 760 nm to 1,200 nm:

General formula (1):  $X^-M^+$

wherein in the general formula (1),  $X^-$  represents an anion containing at least one substituent having an alkali-dissociating proton; and  $M^+$  represents a counter cation which is an atomic group having an absorption maximum at a wavelength in a range of 760 nm to 1,200 nm.

[SELECTED FIGURE]

None